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INVESTIGATION OF AN ENERGY
CONVERSION DEVICE

Report No. 4
Final Report
Contract No. DA 36-039 SC-87229
Task No. 3A99-09-001-02

1 July 1961 to 30 June 1962

U.S. Army Signal Research
and Development Laboratory
Fort Monmouth, New Jersey

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SEPTEMBER 1962

AEROJET-GENERAL CORPORATION
Azusa, California

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INVESTIGATION OF AN ENERGY CONVERSION DEVICE

Report No. 4

1 July 1961 to 30 June 1962

SIGNAL CORPS CONTRACT NO. DA 36-039 SC-87229

Task 3A99-09-001-02

Aerojet-General Final Report No. 2346

SIGNAL CORPS TECHNICAL REQUIREMENT

SCL-2101-K, 20 April 1959

SEPTEMBER 1962

OBJECTIVE

The object of this program is to demonstrate the feasibility of a thermally regenerative energy conversion device in which bismuth triiodide is decomposed thermally to liberate bismuth and iodine, which then separate and ionize at their respective electrode surfaces, producing an electric current. The ions recombine to form the bismuth triiodide, thereby completing the regenerative cycle.

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CONTENTS

	<u>Page</u>
I. PURPOSE _____	1
A. Introduction _____	1
B. Description of Work _____	1
II. ABSTRACT _____	1
III. CONFERENCES AND REPORTS _____	2
A. Conferences _____	2
B. Reports _____	2
IV. FACTUAL DATA _____	3
A. Demonstration of Basic Cell Operation in the Absence of Oxygen _____	4
B. Ceramic Adhesion and Structural Stability Tests _____	10
C. Fabrication of Cells Sealed with Ceramics _____	10
D. Fabrication of Cells with Metal Seals _____	15
E. Fabrication of Composite Cells _____	16
F. Definitive Evaluation of Sauereisen-Sealed Cells _____	23
G. Fabrication of Model Battery for Delivery to USASRDL _____	29
H. Evaluation of Miscellaneous Sealing Techniques _____	30
I. Decomposition Studies with Bismuth Triiodide _____	31
J. Efficiency of Wafer Cells _____	32
K. Reaction Mechanism for Decomposition of Bismuth Triiodide _____	36
L. Operation in Space Environment _____	37
V. CONCLUSIONS _____	40
A. Introduction _____	40

CONTENTS (cont.)

	<u>Page</u>
B. Background _____	41
C. Aerojet Proprietary Development _____	41
D. Work Sponsored by USASRDL _____	43
VI. OVERALL CONCLUSIONS _____	45
VII. RECOMMENDATIONS _____	46
VIII. IDENTIFICATION OF PERSONNEL _____	46
A. Level of Effort _____	46
B. Personnel _____	47
References and Bibliography _____	49
	<u>Table</u>
Examination of Potential Thermally Regenerative Reagents in Electrolyte No. 11 _____	1
Examination of Potential Thermally Regenerative Reagents in Electrolyte No. 12 _____	2
Evaluation of Wafer-Type Cell Utilizing Electrolyte No. 14 + Bismuth Triiodide _____	3
Regenerative Galvanic Cells Operated in Air _____	4
Regenerative Galvanic Cells Operated in Argon _____	5
Regenerative Galvanic Cells Operated in Argon _____	6
Ceramic Adhesion and Structural Stability Test _____	7
Materials of Construction Summary for Cells A-1 Through A-22 _____	8
Evaluation Data from Cell A-5 _____	9
Evaluation Data from Cell A-6 _____	10

CONTENTS (cont.)

	<u>Table</u>
Evaluation Data from Cell A-7 _____	11
Evaluation Data from Cell A-8 _____	12
Evaluation Data from Cell A-9 _____	13
Evaluation Data from Cell A-10 _____	14
Data Summary of Cell Load Characteristics (Cells A-23 Through A-25) _____	15
Data Summary of Thermogalvanic Cells A-23 Through A-25 _____	16
Chemical Analysis of Cell No. 30 _____	17
Current Density Comparison Between Cells Using Electrolytes No. 12 and No. 14 _____	18
Oxygen Data at Time of Argon Shutoff _____	19
Data Summary of 20-Cell Test _____	20
Data Summary of Load Checks for Cells of Different Sauereisens in 20-Cell Test _____	21
Data Summary of Voltage - Time for Cell No. 6 of 20-Cell Test _____	22
Data Summary of 20-Cell Test After 48 Hours Operation _____	23
Materials of Construction of Cell Nos. 59 Through 71 _____	24
Open Circuit and Load Characteristics of Cell No. 59 _____	25
Open Circuit and Load Characteristics of Cell No. 60 _____	26
Open Circuit and Load Characteristics of Cell No. 61 _____	27
Voltages and Current Densities at Various Loads for Cells Nos. 62 Through 66 _____	28
Voltages and Current Densities at Various Loads for Cells Nos. 67 Through 71 _____	29
Open Circuit and Load Characteristics of Silicon Carbide Coated Cell _____	30

CONTENTS (cont.)

	<u>Table</u>
Sublimation of Materials in High Vacuum _____	31
Sublimation of Metals at 1000°C _____	32
Life of Coatings _____	33
	<u>Figure</u>
Basic Regenerative Thermogalvanic Cell _____	1
Effect of Temperature on Power Density _____	2
Sketch of Cell Used for 20-Cell Test _____	3
Apparatus for Testing Regenerative Cells in Argon _____	4
Comparison of Cells Operated in Argon and in Air _____	5
Sketch of Lava Test Cell A-3 _____	6
Sketch of Test Cell A-5 _____	7
Sketch of Test Cell A-6 _____	8
Sketch of Test Cell A-8 _____	9
Sketch of Test Cells A-12 - A-13 _____	10
Regenerative Thermogalvanic Cell with Metal to Metal Seal _____	11
Regenerative Thermogalvanic Cell with Metal to Ceramic Seal (Type 1) _____	12
Regenerative Thermogalvanic Cell with Metal to Ceramic Seal (Type 2) _____	13
Regenerative Thermogalvanic Cell with Metal to Ceramic Seal (Type 3) _____	14
Evaluation of Cell 23 _____	15
Argon Test Apparatus _____	16
Evaluation Apparatus of 20-Cell Test _____	17
Thermal Energy Converter, Schematic _____	18

CONTENTS (cont.)

	<u>Figure</u>
Theoretical EMF vs Temperature of Idealized Thermal Energy Converter _____	19
Theoretical Vapor Pressure vs Temperature of Idealized Thermal Energy Converter _____	20
Idealized Regenerative Thermogalvanic Fuel Cell _____	21

APPENDIX - THERMODYNAMIC CONSIDERATIONS

Distribution List

I. PURPOSE

A. INTRODUCTION

The object of this program is to demonstrate the feasibility of a thermally regenerative energy conversion device in which bismuth triiodide is decomposed thermally to liberate bismuth and iodine, which then separate and ionize at their respective electrode surfaces, producing an electric current. The ions then recombine to form the original metal halide, thereby completing the regenerative cycle.

B. DESCRIPTION OF WORK

The following is a description of the development program by phases:

PHASE I: Electrochemical measurements of open cells and screening of candidate materials to determine their thermochemical properties.

PHASE II: Testing of open cells under various conditions and examination of materials of construction.

PHASE III: Design of sealed cells.

PHASE IV: Construction and test of sealed cells.

PHASE V: Construction and test of sealed cells for battery application.

II. ABSTRACT

Using bismuth triiodide as the material to be thermally decomposed, cells have operated in air for 4 hours at current densities up to 133 mamp/cm^2 at 0.2 v. Similar open cells have operated in argon at a somewhat lower output (caused by lower operating temperature) for 120 hours.

Sealed cells have operated in air for 230 hours. Their regenerative operation has been unequivocally demonstrated.

The major problem remaining in the development of the battery for space use over extended periods of time is the development of satisfactory materials of construction for the individual cell.

III. CONFERENCES AND REPORTS

A. CONFERENCES

1. Aerojet personnel visited Fort Monmouth on 25 July 1961. A general discussion of the program was held. It was agreed that the first tests would be for the purpose of demonstrating that the cells will function when oxygen is excluded by operating them in an atmosphere of argon. It was further agreed that priority would be given to the demonstration of the mode of operation of the cell and the technique of sealing it for operation in outer space.

2. Mr. G. J. DiMasi, the Signal Corps Project Engineer for this contract, visited the Azusa Aerojet facilities on 16 November 1961. A presentation of the program development was made by Aerojet personnel. The presentation included the work thus far accomplished, and an outline for future work. It was concluded that Aerojet had demonstrated that the proposed thermally regenerative fuel cell does operate in the absence of oxygen. It was also concluded that the mode of operation proposed by Aerojet had been substantially verified. It was agreed that priority for future work would be given to devising techniques for sealing cells and testing the feasibility of this system as a thermally regenerative fuel cell.

3. Aerojet personnel visited Fort Monmouth on 23 February 1962. A general discussion of the program was held. It was concluded that a cell should be run in argon at a higher temperature in order to attain current densities of the order of magnitude of 100 ma/cm^2 . Also a comparison would be made between data taken from some early Aerojet tests and cell tests made during present program.

B. REPORTS

Informal monthly letter reports were submitted as follows:

Report No. L-0528-01-1, dated 31 July 1961
Report No. L-0528-01-2, dated 31 August 1961
Report No. L-0528-01-3, dated 30 September 1961

Report No. L-0528-01-4, dated 31 October 1961
Report No. L-0528-01-5, dated 30 November 1961
Report No. L-0528-01-6, dated 31 December 1961
Report No. L-0528-01-7, dated 31 January 1962
Report No. L-0528-01-8, dated 28 February 1962
Report No. L-0528-01-9, dated 31 March 1962
Report No. L-0528-01-10, dated 30 April 1962
Report No. L-0528-01-11, dated 31 May 1962
Report No. L-0528-01-12, dated 30 June 1962

Quarterly reports were submitted as follows:

Report No. 0528-01-1, dated 30 September 1961
Report No. 0528-01-2, dated 31 December 1961
Report No. 0528-01-3, dated 31 March 1962

IV. FACTUAL DATA

The properties of chemical compounds required for use in a closed-cycle thermogalvanic generator are listed in detail in Reference 1. The elements of the compound must be sufficiently differentiated to be separable by heat, and of being recombined in a cell so that the original compound is reformed and an electric current is produced. Bismuth triiodide decomposes at 500°C ; the iodine formed has a boiling point of 183°C , the bismuth one of 1470°C , so they can be separated by distillation. Aerojet developmental work concentrated on the testing of thin wafer-type cells not requiring gravity (see Figure 1).

A number of metallic iodides will operate in the manner of bismuth triiodide in the wafer-type cells. Table 1 shows the voltage developed from a selected group of these salts when dissolved in an iodide-free electrolyte.* Table 2 shows comparable data for a lower melting electrolyte. Figure 2 shows the effect of temperature on power density for representative reactants, and the additive effect of certain reactants used together. In previous work, the wafer cells were developed to the point where a voltage of 0.20 v was obtained at a current density of 135 milliamp per sq cm of extended electrode surface (see Table 3), operating for a short time in air, losing iodine to the air and oxidizing the bismuth.

*The electrolytes used are proprietary in nature, and their formulas are not available at this time.

A. DEMONSTRATION OF BASIC CELL OPERATION IN THE ABSENCE OF OXYGEN

When thermally regenerative thermogalvanic cells using bismuth triiodide as the active agent are tested in air, there is the possibility of oxygen reaching the anode surface even in a supposedly sealed cell. If oxygen does reach the anode surface, there is the second possibility that part of the voltage developed could be attributed to oxygen. To prove that the voltage developed in cells using bismuth triiodide is a result of the bismuth triiodide cycle and not of oxygen depolarization, a series of tests were run in an inert, argon atmosphere.

1. Detailed Description of the Battery

a. Cell Description

A typical cell comprises two thin disks of graphite or other electrode material located on either side of a layer of absorbent material which is impregnated with an electrolyte containing the bismuth triiodide. The approximate dimensions of these uncoated cells which were used in the early work were 1 in. dia x 3/16 in. thick. During operation, the temperatures of the two electrodes were measured by means of thermocouples in contact with their outer surfaces. Electrical contact was made by various means, such as spring members or friction contact of wire leads in holes in the electrodes. In many cases, contact was made to a tab on the electrode which extended out of the zone of maximum heat.

b. Preparation of Electrolyte Layer

The requisite electrolyte salts were dissolved in water. Bismuth triiodide was then added to this solution in a finely ground state. This solution was used to completely saturate a piece of 1/4-in. Fiberfrax (a synthetic, asbestos-like material). The Fiberfrax was then dried in a vacuum oven at 130 to 140°C, and held under these conditions until incorporation in a cell for testing. The preparation of the electrolyte and Fiberfrax pads was the same for all tests except Cell 3, described in Section V,A,3, in which bismuth triiodide was not used.

2. Test Apparatus

a. Control Tests in Air

For tests in air, the cells were supported by a nickel plate, which in turn was placed on a heat source. To measure the surface temperature

of the electrodes, thermocouples were placed in contact with them. Cell voltages were measured by means of a Simpson multimeter, and the temperatures were measured by means of a Leeds and Northrup potentiometer. Pressure to ensure contact between cell components, electrodes, and impregnated Fiberfrax was applied to the top side of the cell by means of a carbon rod supported by a ring and clamp.

b. Tests in Argon

The initial apparatus for testing cells in an argon atmosphere was essentially the same as that described above for operation in air, except that the complete assembly was placed in a desiccator, which was then sealed. The thermocouples, voltage taps, argon inlet and outlet, etc., were sealed in an opening in the desiccator lid by a rubber stopper and Sauereisen cement. In these tests, argon was streamed through the desiccator. The argon outlet was fitted with a potassium iodide trap to determine if any iodine was swept from the desiccator. Temperatures were recorded on a Leeds and Northrup potentiometer, and the voltages were recorded on an Esterline-Angus recording voltmeter. Because of difficulties encountered in the operation of this system, a more refined apparatus was designed for further testing.

In the modified apparatus, the desiccator was replaced by a resin kettle. Figure 4 is a photograph of two assemblies. The seal between the resin kettle lid and the body was made using silicone high-vacuum grease. The voltage taps, thermocouples, heater leads, carbon rod, and argon inlet and outlet were sealed in the holes in the resin kettle lid with Sauereisen cement. The carbon rod was threaded so that by turning it clockwise, pressure could be applied to the cell to maintain contact between the electrolyte layer and the electrodes. The top portion of the carbon rod was sealed with Sauereisen cement. To ensure a complete seal against air, an ample coating of silicone grease was applied over all the Sauereisen cement seals.

A further modification of the argon test apparatus was used with Cells 30 through 37, which are described later. The conventional air test apparatus was placed on a 22 x 22 x 1/4-in. steel plate. This apparatus was then covered by inverting a 16-in. dia. 12-in.-high glass battery jar over it. A seal

was effected by a rubber gasket between the jar and the steel plate. Permatex No. 2 gasket sealing material was also used between the rubber and glass. Thermocouples, electrical contacts, argon inlet and outlet, and the heater element electrical lead passed through holes drilled in the steel plate. These holes were sealed with No. 8 Sauereisen cement. The argon outlet passed through a trap containing potassium iodide solution.

3. Cell Tests

a. Unsealed Cells in Air

The first cells tested in this work were unsealed and exposed to air. Table 4 shows the results of these tests. The voltages recorded are the maximum obtained on a 33-ohm load. These results compare favorably with previous work done under Aerojet sponsorship.

b. Sealed and Unsealed Cells in Argon

The initial test in argon was made with an unsealed cell in a desiccator to determine operating characteristics under these conditions, but due to difficulties encountered in operation, no experimental data was obtained.

The second test in argon was made with an unsealed cell in a resin kettle. The duration of the test was 121 hours. The cell was operated for the first 2 hours at approximately 679°C at the hot electrode, with an argon flow of 600 ml/min to remove water and air from the apparatus. During the next 16 hours, the temperature was reduced to 170°C and the argon flow was maintained to keep the cell dry and air-free. For the next 28 hours, the temperature was held around 690°C at the same argon flow. The argon flow was then stopped to limit the quantity of oxygen* available to the cell, and the temperature was held around 650°C for the remaining 75 hours. Table 5 shows the results of this test.

At the conclusion of the experiment there appeared to be a considerable amount of bismuth triiodide on the walls of the resin kettle. Near the conclusion of the test, the voltage decreased, indicating loss of bismuth

*The argon used had a maximum oxygen content of 5 ppm.

triiodide from the cell. The KI-solution was analyzed for iodine. A quantity was collected which amounted to about one-third of that originally present in the bismuth triiodide. This demonstrated that bismuth triiodide was decomposed by heat, and that some of the released iodine was lost from the cell.

Additional experiments were made using two resin kettles so that two cells could be operated simultaneously. One cell was unsealed and the other cell was sealed around the edges with Sauereisen cement. The results of this experiment are presented in Table 6 under Cells No. 1 and 2.

There was intermittent flow of argon (600 ml/min) for the first 24 hours to ensure complete removal of water and air from the apparatus. After 24 hours, both cells operated under a static atmosphere of argon until the termination of the experiment. The oxygen content of the argon used was 3 ppm, as determined by the titanium chloride method. It was calculated that at the time the argon flow was shut off, there was 0.012 ml of oxygen present in each system. Based on an output calculated from the recorded voltages and the measured resistance of the external circuit, this amount of oxygen would have been sufficient to operate the unsealed cell for a maximum of only 9.5 min, and the sealed cell for 12 min. The unsealed cell operated for approximately 60 hours after the argon flow was shut off and the sealed cell operated for 56.6 hours. Since neither cell in this experiment was completely sealed, they were operated at less than optimum conditions in order to ensure 48-hour operation in a static atmosphere of argon. The presence of the seal appears to have reduced the loss of the iodine. The lower output of the sealed cell may have been caused by the rigid cement preventing the maintenance of good contact between the cell components.

After 49 hours of operation in a static atmosphere, the cells were intermittently subjected to increasing loads. Figure 5 shows the relationship of voltage and current density for the unsealed cells operated in argon and in air. Several times throughout the experiment, additional pressure to maintain contact between cell components was applied to the cells by means of the threaded graphite rod. These increments of pressure did not cause any alternations in the voltage output of either cell. Just prior to terminating the experiment, air was admitted to each resin kettle. In each case, the voltage dropped to zero, then

there was a slight reversal of polarity. This may have been due to the fact that the cell was operated with oxygen as the depolarizer for the hot electrode when air was admitted. This action confirmed earlier observations that oxygen is detrimental to proper cell operation. At the termination of the experiment, both traps were examined and 21.6% of the iodine was found in the trap for the unsealed cell and 6.1% for the partially sealed cell. There was no evidence of the presence of iodine within either resin kettle. However, deposits observed on the walls of the resin kettle did contain bismuth triiodide and, probably, electrolyte compounds.

Inspection of the cells at the termination of the experiment showed the Fiberfrax to be white and dry, indicating essentially complete loss of the electrolyte. There was also considerable loss of graphite from the anodes (hot side) in both cells. Both anodes measured 1 in. dia at the beginning of the experiment. At the termination of the experiment, the anode in the unsealed cell measured 1/4-in. in dia, while the anode in the partially sealed cell measured 5/8-in. A metallographic examination of the nickel revealed a definite increase in grain size at the surface. This increase in grain size may be attributable to carburization; however, further work did not support this hypothesis.

In another pair of experiments, a completely sealed cell containing bismuth triiodide, and an unsealed cell with bismuth triiodide omitted from the electrolyte, were operated simultaneously. The data for the operation of these cells are recorded in Table 6 under Cells No. 3 and 4. With the unsealed cell, the argon flow was maintained for 33 hours. With the sealed cell, flow was for 28 hours. This flow of argon, as before, was to flush moisture and air from the apparatus. The oxygen content of the resin kettles was 0.012 ml at the time of argon shutoff. Estimated from data obtained during the run, this amount of oxygen would have been sufficient to operate the sealed cell for no longer than 3.5 min. The cell operated for 137 hours after the argon flow was shut off. The static atmosphere of argon was maintained throughout this period. Because the unsealed cell, with no bismuth triiodide present, did not function, no time for its oxygen consumption is given in Table 6. Although some small voltages were recorded, these may be attributable to concentration or thermal phenomena.

The completely sealed cell was encapsulated in three layers of ceramic. The first layer was Astroceram, the second layer was Sauereisen, and the third and final layer was Astroceram. After the application of each layer of Astroceram, the cell was fired at 1100°F to harden the ceramic. The Sauereisen layer was air-dried overnight. The low output of this cell, as compared to the two cells of the previous test, is attributed to loss of electrolyte during the firing of the ceramic coatings.

Applying pressure on Cells No. 3 and 4 to assure contact of cell components did not cause any change in voltage for either cell. At the termination of the experiment, the traps had collected 7.4% of the original quantity of the iodine from the unsealed cell, and none from the sealed cell. Visual observations indicated that bismuth triiodide had been deposited on the walls of No. 3 resin kettle.

Inspection of the cells at the termination of the experiment showed complete loss of the graphite anode and partial loss of the graphite cathode for the unsealed cell. The graphite anode and cathode of the sealed cell showed no loss. The structural stability of the sealed cell was good. There was no chalking or cracking of the ceramic coating. The coating was solid and did not crumble or break until considerable pressure had been applied.

4. Discussion

The test in argon proved that thermally regenerative thermogalvanic cells using bismuth triiodide as the active agent operated as well in the absence of oxygen as in its presence. It was also proved that bismuth triiodide, the postulated active agent, was necessary for cell operation. It was also shown that bismuth triiodide decomposes on the application of heat, as evidenced by the presence of iodine in the potassium iodide trap. These tests verified the postulated reaction mechanism; the decomposition of bismuth triiodide by thermal energy into bismuth and iodine, followed by ionization of these elements generating an electric current; then combination of the ion species to again form bismuth triiodide, thus completing the cycle. These tests conclusively proved that the bismuth triiodide system does not involve an oxygen electrode.

B. CERAMIC ADHESION AND STRUCTURAL STABILITY TESTS

Having proved the mechanism of cell reaction, and that the system does not need oxygen to operate, the next logical step in the development of sealed cells for space application was the screening of materials for sealing that would be compatible with the electrochemical system.

Various ceramics were checked for adhesion to graphite and nickel, and for structural stability at elevated temperatures (700 to 900°C). The following is a list of the ceramics tested:

	<u>Ceramic</u>	<u>Source</u>
1.	Sodium Silicates	Philadelphia Quartz Co. of Calif.
2.	Astrocerams	Astroceram Co.
3.	Baymal	E. I. duPont de Nemours
4.	Typersul	E. I. duPont de Nemours
5.	Typersul + Baymal	E. I. duPont de Nemours
6.	Sauereisen No. 29	Sauereisen Company
7.	Lava (structural stability test only)	American Lava Corp.

Table 7 shows the results of these tests. Of the materials tested, Lava and Astroceram appeared to be the most promising.

Silver paint, No. SCP-12, obtained from the Micro-Circuits Company, was tested in air at approximately 800°C as a sealing agent between nickel and Lava, and between Lava and Lava. This type of seal appeared to be very satisfactory.

C. FABRICATION OF CELLS SEALED WITH CERAMICS

From the results of the structural stability and adhesion tests, a group of ceramics were chosen to be tested as sealing agent in cell fabrication.

1. Astroceram

One of the first ceramics to be tested which proved to be satisfactory in the stability and adhesion test was Astroceram, a product of the Astroceram Co.

Two cells, A1 and A2, were constructed using Astrocerams of BLP and ALP grades as sealing agents; these cells were tested for porosity under conditions of cell operation. Table 8 gives the data summary of the materials of construction for these cells.

Graphite was used as the electrode material. One cell was sealed with BLP grade Astroceram; the other cell was sealed with the ALP grade. Fiberfrax, impregnated with electrolyte, was sandwiched between the electrodes and the entire assembly was encapsulated with the sealing agent. No electrical leads were incorporated and no load was applied. The cells were heated in air at temperatures from 700 to 800°C.

The two cells were structurally sound at the temperatures tested. However, loss of electrolyte was indicated by discoloration of the Astrocerams, and destructive inspection of cells after testing showed that most of the electrolyte and product had boiled out. This indicated that the Astrocerams were too porous for use as sealing agents.

2. Lava

Because of the porous nature of the Astrocerams, several different designs of cells using Lava for cell containers and silver paint as the sealing agent were constructed. Information indicated the Lava to be impervious after firing at 1100°C. The Lava containers were fabricated and fired prior to cell assembly. From the stability and adhesion tests it was known that the silver paint to be used as the sealing agent was satisfactory for use on both nickel and Lava.

a. Group One

Cells A3 and A4 were constructed using graphite electrodes; Lava for the cell container, and silver paint No. SCP-12 for the sealing agent. Table 8 gives the data summary for the materials of construction used in fabricating these cells. Fiberfrax was used as the electrolyte carrier. Figure 6 is a diagram of this type of cell. Electrical contact was made by means of a fired gold coating on the Lava plugs, as shown in the figure. These cells operated in air at temperatures up to 750°C. Erratic voltages were obtained; because of poor electrical contact, the tests were terminated after 54 hours. Loss of the electrolyte and product from these cells was not determined.

b. Group Two

Cells A5 and A6 were constructed with an improved method of making electrical contact with the electrodes. Materials of construction data is given in Table 8. Both cells had nickel anodes and graphite cathodes. Lava was used as the cell container; No. SCP-12 silver paint was used as the sealing agent. Fiberfrax served as the electrolyte carrier. The following methods of making electrical contact with the electrodes were used: the Lava anode plug was replaced by a nickel plug which served as the anode, and direct electrical contact could be made; in Cell A5, the graphite cathode served as the cathode plug, and a direct electrical contact could be made; in Cell A6 the cathode electrical contact was made by a nickel screw threaded through the Lava plug, making contact with the graphite cathode. Figures 7 and 8 are diagrams of Cells No. A5 and A6, respectively.

These cells operated at voltages comparable to those of the cells tested in argon. Cell No. A5 operated for 120 hours, while Cell No. A6 operated for 91.5 hours. Both tests were terminated by cracking of the Lava case, resulting from the difference in thermal expansion of the nickel and Lava. The difference in life is attributable to the difference in design at the junctions of the anodes and cases. Inspection of these cells after testing showed loss of electrolyte. The electrolyte loss might have been caused by leakage through the cracked case or by absorption by the porous graphite and the ceramic. Tables 9 and 10 show the results of these tests. In spite of the mechanical difficulties encountered, the outputs of the cells were superior to those shown for the cell of Table 4 at comparable loads and temperatures.

c. Group Three

On the assumption that the major loss of electrolyte in Cells A5 and A6 was caused by absorption in the Lava, Cell A7 was constructed using a new ceramic as the sealing agent, Sauereisen Cement No. 7. Materials of construction data for this cell are given in Table 8. Cell A7 was constructed the same as Cell A6 except that the entire cell assembly was encapsulated with the sealing agent. This cell operated satisfactorily in air for 144 hours before the Lava container cracked at the metal electrode. No loss of electrolyte due to the porosity of the Lava and the sealing agent was noted up to the time the case cracked. The data are shown in Table 11.

3. Sauereisen

In previous tests, all failures were attributed to either loss of electrolyte because of the porosity of sealing agent, or cell fracture caused by differences in thermal expansion of electrode material and sealing agent. Several cells were constructed using Sauereisen Cements as sealing agents. The cells were designed to eliminate the above mentioned reasons of cell failure.

a. Group One

In Cells A8 and A9 the nickel anodes were replaced by graphite and two new Sauereisen cements were used as sealing agents. Material of construction data for these cells is given in Table 8. Sauereisen Cements No. 32 and No. 7 were used to seal Cells A8 and A9, respectively. Fiberfrax was used as the electrolyte carrier in both cells. The cells were encapsulated with the sealing agent, as shown in Figure 9. Cell A8 operated for 172 hours, while Cell A9 operated briefly after an idle time of 148 hours. The electrical outputs of these cells are recorded in Tables 12 and 13.

In these cells, which used Fiberfrax as the electrolyte carrier, it was noted that to maintain good electrical output, increasing increments of energy (increasing operating temperature) were needed. A destructive inspection of Cell A8 showed that this decline may have been caused either by absorption into the porous graphite and ceramic, by collapsing of the Fiberfrax pad and the resultant loss of contact between it and the electrode surface, or by both of these processes.

b. Group Two

Cell A10 was designed to eliminate loss of contact between the electrolyte and the electrode surfaces due to collapsed absorbent layer. Summary of material of construction for this cell is given in Table 8. The cell used Sauereisen Cement No. 32, as the sealing agent, and the anode and cathode were both graphite. In this cell the impregnated Fiberfrax pad was replaced with a non-compressible, impregnated porous ceramic disc. The ceramic used for the disc was Sauereisen Cement No. 29. The impregnated disc and electrodes were encapsulated with the sealing agent. The cell operated favorably for 24 hours before the ceramic was destroyed at its point of contact with the heat source. The data for this cell are recorded in Table 14.

c. Group Three

Cell All was designed to eliminate absorption of electrolyte into the porous graphite electrode. This cell used Fiberfrax as the electrolyte carrier. The construction of this cell was the same as Cell A8 (Table 8 gives the materials of construction data) except that the electrodes were impregnated with electrolyte prior to encapsulation. This cell developed leaks at the point where the leads entered the ceramic, and a crack developed along the side before a significant voltage was recorded. The electrolyte on the electrodes interfered with the proper functioning of the ceramic seal.

4. Nickel

In all previous cells tested, the material used to seal the cells has been composed entirely of ceramic materials. All of these materials have been porous to some degree. In order to reduce the loss of electrolyte and bismuth triiodide through the porous ceramic, thereby increasing cell operating life, a cell was designed using a nickel cup. This nickel cup served as the anode and cell container. This type of construction reduced the amount of ceramic required for sealing by better than 50%.

Cells A12 and A13 were designed to extend cell life by reducing loss of electrolyte through the ceramic. Table 8 gives the materials of construction data. These cells were also designed to eliminate loss of contact between the compressible Fiberfrax pad and the electrode surfaces. Nickel cups were used as both anode and container and the carrier material was eliminated from the electrolyte layer. Figure 10 is a diagram of this type of cell. To electrically insulate the nickel anode from the graphite cathode, the insides of the walls of the cups were lined with Crystal M, a synthetic mica sheet made by the Minnesota Mining and Manufacturing Company. Approximately 1/8 in. of dry, powdered electrolyte plus bismuth triiodide was added to the lined nickel cups. Heat was applied to the cups to melt the electrolyte. As soon as the electrolyte became fluid, the graphite cathodes were put in place on the fluid electrolyte, and the cells were sealed with Sauereisen Cement No. 29 and coated with Cement No. 32. The cells operated intermittently for approximately 168 hours. Voltages recorded were very erratic, and the data are not presented in this report. These lower voltages are attributed to poor contact

resulting from loss of electrolyte by absorption into the graphite and ceramic. Cells A14 and A15 were constructed and tested. The former cell has graphite electrodes separated by a ceramic ring and contains no electrolyte carrier. This assembly is encapsulated with Sauereisen Cement No. 32. The latter cell also has two graphite electrodes. The sealing material is a new polymeric silicate developed at Aerojet. This cell used Fiberfrax as the electrolyte carrier. Both of these cells showed signs of leaking on the application of heat, and the test was stopped after several hours. No data was recorded for these cells.

5. Discussion

The cell tests have been terminated because of either loss of electrolyte and bismuth triiodide through porous ceramic materials used in construction, or through cracks developing usually at the metal-to-ceramic interface. These cracks develop because of the difference in expansion between the ceramic and metal. Several new methods of construction were undertaken.

D. FABRICATION OF CELLS WITH METAL SEALS

As previously mentioned, the major cause of the termination of cell tests has been caused by loss of electrolyte and bismuth triiodide through either the porous ceramics or cracks at the metal-ceramic interface caused by difference in thermal expansion. To eliminate this loss of electrolyte, a cell has been designed incorporating commercially available, non-porous ceramic-to-metal seals, and Heliarc or silver solder metal-to-metal seals made in the laboratory. This type of construction is designed to eliminate loss of electrolyte through porous ceramic materials.

1. Cell Description

Figure 11 shows the type of construction used in preparing cells having laboratory metal-to-metal seals. Non-porous metal-to-ceramic seals were obtained commercially, to be used as the electrical lead from the cathode. A nickel cup served as both anode and cell container. The inside walls of the cup were insulated with a paper-thin synthetic mica (Crystal M) manufactured by the Minnesota Mining and Manufacturing Company. A nickel cover was silver-soldered or welded by Heliarc to the nickel container. Sealed into the nickel cover by the same processes were the electrical cathode lead, and, when necessary, a tube

for filling the cell with electrolyte. Two types of cathode leads were used; one manufactured by the American Stoneware Company, a tubular electrical lead through which the cell was filled; the other lead used was a glow-plug type. When the glow-plug-type lead was used, a tube was soldered into the cover through which the cell could be filled with electrolyte. The graphite cathode was attached to the electrical cathode lead. On the top of the cathode was a layer of Crystal M paper. In some cells, the underside of the nickel cover was coated with a layer of insulating Sauereisen cement. After the cover was sealed to the container, molten electrolyte and bismuth triiodide were added to the cell through the tubes. These tubes were then crimped shut and sealed with silver solder.

2. Cell Tests

Seven cells (Nos. 16 through 22) using commercial metal-to-ceramic seals and laboratory metal-to-metal seals were constructed and tested in air. All of these cells were found unsatisfactory because of leaks at the metal-to-metal seals or at the electrical cathode leads, or because of shorted cells. The intense heat of the Heliarc and silver-solder (+900°C) processes used in making the laboratory metal-to-metal seals are sufficient to destroy the non-porous, commercial metal-to-ceramic seals, causing shorted cells and leaks. No data were recorded for these cells, as the leaks became evident shortly after heat was applied to the cells. All cells with metal-to-metal seals tested in this laboratory were inoperative because the commercial ceramic-to-metal seals were destroyed by the intense heat of the Heliarc or silver-solder process used to make the laboratory metal-to-metal seal.

E. FABRICATION OF COMPOSITE CELLS

Because of difficulties involved in making laboratory metal-to-metal seals, several cells of new design were constructed using metal-to-ceramic seals. The ceramic used in sealing these cells was Sauereisen Cement No. 29. This ceramic had been used in previous cell construction, and had proved to be porous. Attempts were made to make the Sauereisen impervious by glazing; that is, by mixing it with small pieces of glass wool.

1. Cell Description

a. Type 1

Figure 12 shows the construction used in this type of cell. They contain metal anodes and cathodes. The cathodes were fabricated from either

molybdenum or tungsten. Nickel was used for the anodes. The tungsten or molybdenum was formed into shallow cups, while the nickel was punched into a smaller diameter disc. A piece of Fiberfrax (carrying the electrolyte) was placed in the molybdenum or tungsten cup, and the nickel disc was placed on top of the Fiberfrax. Sauereisen cement was used to seal the annular space between the anode and cathode. The Sauereisen cement served as both a sealing agent and the insulator.

b. Type 2

The construction of this cell is shown in Figure 13. In this type of cell the cathode was graphite and the anode was nickel. The sealing agent was Sauereisen cement and the insulator was Coors Volcanous ceramic. The insulator ring was placed inside the nickel anode, which was fabricated in the shape of a cup. The Fiberfrax (carrying electrolyte) and the graphite cathode was fitted inside the insulator ring. Sauereisen cement was used to seal the insulator ring to the nickel anode and the graphite cathode.

c. Type 3

Figure 14 shows the construction of this type of cell. Essentially, it is similar to that of Type 1. Type 1 used a tungsten or molybdenum cathode while the cathode in Type 3 was graphite, which was cemented to the underside of the molybdenum or tungsten cup by means of Thermon, an air-drying graphite paste manufactured by the Thermon Manufacturing Company. Fiberfrax served as the electrolyte carrier, and Sauereisen cement served as the sealing agent and insulator.

2. Cell Tests

a. Cells No. A21 and A22

Cells No. 21 and 22 were operated on a 415-ohm load in air. As the tests were initiated, the voltage of the cells rose sharply to a peak voltage of 0.25 v at a temperature of 400°C. The voltage then gradually fell to zero over a period of 20 hours. Destructive inspection of these cells revealed that a non-conductive coating had formed on the cathodes. This coating may have contributed to the poor electrical output. Loss of electrolyte from the cells caused by leakage resulted in termination of the experiment after 20 hours.

b. Cells No. A23

Cell No. 23 was tested in air at an average hot side temperature of 550°C . Voltages were recorded for 148 hours. The average voltage for this period was 0.173 v, with a maximum voltage of 0.46 v on a load of 415 ohms. Figure 15 is a plot of voltage vs time. Table 15 gives the load characteristics for this cell. Also, for comparison the load characteristics of an open-type cell taken from data previously obtained under a company-sponsored program are included in this table. Failure of a heating element caused the temperature of Cell No. 23 to drop 300°C . On reheating, the voltage again rose to its previous value, but the temperature cycle had caused a crack to develop at the ceramic interface and the electrolyte was lost, terminating the test. All construction data and operating life are summarized in Table 16.

c. Cell No. A24

This cell was operated in air on a 415-ohm load. The cell operated for 128 hours at an average voltage of 0.145 v at a temperature of 500 to 600°C . A maximum voltage of 0.40 v was attained at these temperatures on a 415-ohm load. Table 16 gives the load characteristics of this cell at 500°C . These values were taken 50 hours after the first recorded voltage. The test was terminated after 128 hours because cracks developed at the metal-to-ceramic interface. Data for this cell are recorded in Tables 15 and 16.

d. Cells No. 25 and 26

Cells No. 25 and 26 were identical in construction. In this experiment, one cell was held to a low temperature (550 to 650°C) and load (415 ohms) while the other cell was taken to 900°C and subjected to various loads at 50°C increments in the hot-side temperatures of from 550 to 900°C . Due to radiation effects and inadequate insulation, the maximum temperature attained on the hot side was 721°C . Data for these cells are recorded in Tables 15 and 16. Cell No. 25 operated for 168 hours. At a hot-side temperature of 553°C and a load of 50 ohms, this cell developed 0.11 v with a current density of 0.68 milliamp/sq cm. Cell No. 26 had an operating life of 168 hours. At a hot-side temperature of 666°C and a 50-ohm load, this cell developed 0.09 v with a current density of 0.56 milliamp/sq cm. Termination of this experiment was caused by cracks which developed at the ceramic-to-nickel interface and the ceramic itself. This resulted in loss of electrolyte and bismuth triiodide from the cell.

e. Cells No. 27 and 28

Cells No. 27 and 28 were identical in construction and were operated in air on a 415 ohm load. Voltages on other loads were read several times during the test. Cell No. 27 developed 0.21 volt on a 50 ohms load giving a current density of 1.31 milliamps/sq cm. This voltage was developed at a hot-side temperature of 630°C. The operating life of this cell was 43 hours. Cell No. 28 operated on a 415-ohm load for 24 hours, with voltage readings being made at various loads several times during this period. The cell developed a maximum voltage of 0.13 v on a 415-ohm load at a current density of 0.09 milliamp/sq cm. The hot side temperature was 600°C. This cell did not function properly because of poor electrical contact between the electrodes and their electrical leads. Because no appreciable voltage was developed, the test was terminated after 24 hours. Termination of tests on Cell No. 27 was caused by cracks developed at the ceramic-metal interface. The data summary of cell construction and operating life is given in Table 16; the data summary for load characteristics is given in Table 15.

f. Cell No. 29

The loss of electrolyte and bismuth triiodide from cells caused by cracks developing at the metal-ceramic interface has been the major factor governing cell operating life. In Cell No. 29, a thinner-gauge nickel (0.010 in. instead 0.022 in.) anode was used in an attempt to extend cell life by reducing the strain at the metal-ceramic interface. The graphite cathode in this cell was also impregnated with an electrolyte just prior to cell assembly. This cell was operated in air for 48 hours. The cell developed 0.165 v on a 50-ohm load at a current density of 1.03 milliamps/sq cm. The hot side temperature was 567°C. Although a thinner-gauge nickel anode was used in this cell in an attempt to eliminate cracking at the metal-ceramic interface, the termination of this test, as with other metal-ceramic sealed cells, was caused by cracks developing at this interface.

g. Cell No. 30

Cell No. 30 was operated in argon, in an apparatus shown in Figure 16, to ensure that any increase in current density obtained could be attributed to Electrolyte No. 14. The nickel anode was fabricated from 0.005-in. stock in a further attempt to increase cell life by eliminating cracking at the

metal-ceramic interface. Additional dry solid bismuth triiodide was added to this cell just prior to cell assembly. The cathode in this cell was porous carbon No. 20 manufactured by National Carbon Company. Previous cells covered in this report used high-density graphite manufactured by the same company. Two new sealing agents were used, Sauereisen Cements No. 8 and 31. At a hot-side temperature of 740°C , the cell developed 0.46 v on 50 ohms, with a current density of 2.86 milliamp/sq cm. On a 5-ohm load at the same hot-side temperature, this cell developed 0.22 v with a current density of 13.7 milliamp/sq cm.

Table 16 shows that Cells No. 30 through 35, in general, have a shorter life. This shorter life can be attributed to the fact that these cells were heated to high temperatures (800 to 900°C) very rapidly, causing cracks at the metal-ceramic interface in a relatively short period of time. Also, higher operating temperatures probably caused a much faster rate of electrolyte loss through the cracks. To verify the loss of electrolyte from Cell No. 30, an analysis was made of the deposits formed on the walls of the bell jar during test. The cell was opened after test and the Fiberfrax pad was analyzed. Also, a blank analysis was made on a non-impregnated piece of Fiberfrax. The results are presented in Table 17. The presence of Electrolyte components in the deposit taken from the walls of the bell jar are confirmed. This verifies that the loss of electrolyte from Cell No. 30 was the cause of its short life of 29 hours. The use of Electrolyte No. 14 resulted in a marked increase in current density and voltages. Table 18 presents a comparison of current densities at the static voltage and temperatures for Cell No. 30, as well as other cells covered by this report. The use of 0.005-in. nickel for the anode did not eliminate cracking at the metal-ceramic interface. Cell construction data and operating life are given in Table 16. Table 15 gives load characteristics for the cell. Table 19 gives oxygen data at time of argon shut off.

h. Cells No. 31 and 32

In Cells No. 31 and 32, both the cathodes and the Fiberfrax pads were impregnated with molten electrolyte. They were saturated with it just prior to cell assembly. The active agent, bismuth triiodide, was added to the cell in dry solid form just before assembly. These two cells were designed to operate

at high current densities. Also, a study of the effect of impregnating the Fiberfrax pad with electrolyte was to be studied. For comparison, Cell No. 31 was operated in air while Cell No. 32 was operated in an argon atmosphere. Data for these cells are recorded in Tables 15 and 16. Because of the relatively short operating life, 29 hours for Cell No. 31 and 2 hours for Cell No. 32, caused by cracks developing at the metal-ceramic interface, no comparison was made.

i. Cells No. 33 and 34

Cells No. 33 had approximately 4% bismuth triiodide, which is the normal percentage, while Cell No. 34 had 9% bismuth triiodide. Both cells were tested in argon. These two cells were tested with the different percentages of bismuth triiodide to determine if the good load characteristics of Cell No. 30 were due to Electrolyte No. 14, or whether the extra amount of bismuth triiodide was a major contributing factor. Data summarizing cell construction and operating life are given in Table 16. Table 15 gives the load characteristics of the cell and Table 19 presents the oxygen data. As can be seen, Cell No. 33 operated for 35 hours. On 50-ohm loads at 810°C (hot side), it developed 0.221 v at 1.37 milliamp/sq cm. Cell No. 34 developed 0.275 v at 1.71 milliamp/sq cm with a hot-side temperature of 850°C. The cell operated 18 hours. Further tests of these cells under various loads show that Cell No. 34, having a higher percentage of bismuth triiodide, had slightly higher voltages and current densities. However, this difference was so small that the shorter operating life of Cell No. 33 (caused by more rapid loss of electrolyte) could be the cause of this difference.

j. Cell No. 35

The addition of an extra amount of bismuth triiodide did not have an appreciable effect on the cell's electrical output. The effect of the addition of an extra amount of bismuth as bismuth metal was tested in Cell No. 35. Data for this cell was presented in Tables 15, 16, and 19. As can be seen from the data presented in Table 15, the difference between Cells No. 34 and 35 is slight, and could be attributed to experimental error. Termination of this test was, as before, caused by cracks developing at the metal-ceramic interface.

3: Discussion

In the cells employing glass wool in the Sauereisen cement used as the sealing agent, it was impossible to ascertain if the glass wool made the Sauereisen cement impervious. The cell tests were terminated in most cases because of loss of electrolyte and bismuth triiodide through cracks developing at the metal-ceramic interface. These cracks resulted from the difference in thermal expansion between the Sauereisen sealing agent and the metal. In general, the use of Electrolyte No. 14 (Cells No. 30 through 35) greatly improved the operating current density. Increasing the percent of bismuth triiodide in the electrolyte (No. 14) did not show any conclusive evidence of improvement in the cell's operating current density. The shorter operating life of Cells No. 30 through 35 can be attributed to higher operating temperatures.

F. DEFINITIVE EVALUATION OF SAUEREISEN-SEALED CELLS

The termination of most cell tests (outside of mechanical difficulties) has been caused by loss of electrolyte and bismuth triiodide through the pores of the ceramic used or cracks developing at metal-ceramic interface cause by difference in thermal expansion. Laboratory metal seals proved unsatisfactory because the heat developed in making the metal-to-metal seal destroyed the commercially obtained metal-to-ceramic seal. Because the time element of the existing contract and the contract commitment for the delivery of a battery, it was decided to construct cells using ceramics as sealing agents and graphite for electrodes which would eliminate one of the above reasons for cell failure, that of cracks developing at the metal-ceramic interfaces. The first and most logical step was to re-evaluate the sealing properties of some of the better ceramics used. Twenty cells were constructed using five different Sauereisen cements as ceramic sealing agents, and an encapsulating technique was employed in cell construction. This method of construction was chosen so that a continuous film of sealing agent would encompass the cell.

1. Cells Encapsulated With Sauereisen Cements

Twenty cells were tested in air using various Sauereisen cements to confirm results of earlier tests made to determine which cement was the most suitable sealing agent. The Sauereisen cements tested were Nos. 7, 8, 29, 31, and 32. Spectrographic-grade graphite (No. U120) manufactured by United Carbon Products Co., was used for both the anodes and cathodes. The dimensions of the electrodes were 1-1/2 x 1-1/2 x 1/8 in. Fiberfrax was used as the carrier for Electrolyte No. 14. The Fiberfrax pad measured 1 x 1 x 1/4 in. The anode and cathode electrical leads were nickel.

Figure 3 shows a typical cell used in this work. The leads were placed in holes drilled in the edges of the electrodes about 1/4 in. deep. The holes were slightly undersized, the leads were held in place both by friction and by the sealing agent applied to the cell. In the centers of the edges containing the electrical leads holes were drilled to a depth of 3/4 in. to accommodate thermocouples. The insulation on the thermocouple wires was stripped off

3/4 in. from the end, and the bare wires were coated with sodium silicate Type N prior to insertion into the holes in the electrodes. The thermocouples were held in place by the sealing agent. The two holes for accommodating the electrical lead and thermocouple were drilled in each electrode, and then the electrodes were coated on one side and at the edges with the various sealing agents. Eight electrodes were coated with each of the Sauereisen cements mentioned above. These were allowed to air-dry, and then fired at 950°C in a nitrogen atmosphere. The electrical leads and thermocouples were then inserted in the electrodes. The Fiberfrax pads containing Electrolyte No. 14 were sandwiches between two electrodes and sealed around the edges with the same Sauereisen cement used to coat the electrodes. The fabricated, sealed cells were allowed to air-dry, and then glazed with several coats of sodium silicate. The glaze was not fired prior to testing.

The apparatus for testing the cells is shown in Figure 17. The heating elements used in this work were halves of 12-in. tube-furnace elements. Four such halves were used. Each element was cradled in 2 in. of magnesite pipe insulation. The inside diameter of the heating elements was such that the cells could be placed across the top of the element for support. The cells were then heated by radiant heat. As shown by Figure 17, the cells were placed on the elements in contact with one another to reduce heat losses between cells. Five cells, one with each sealing agent, were placed on each of the heating elements. Also, to insure approximately equal radiation on the five test cells, blank cells sealed with Sauereisen Cement No. 29 were placed at the outside of the end test cells. These blank cells are designated by "0" in Figure 17. Fiberfrax pads were placed in the ends of the heating elements to reduce radiation losses at this point. The voltages and anode (hot side) and cathode (cold side) temperatures were monitored individually by means of two, six-gang, twelve-point selector switches. The temperatures were measured by a Brown recorder. The voltages were measured on a Simpson multimeter.

This test was originally designed to test the sealing agents at 600, 700, 800, and 900°C. However, due to heat rejection by the glazed, white Sauereisen cements, the maximum temperature attained on the hot side was 750°C.

Table 20 gives a data summary of open-circuit voltage, and voltages obtained on a 50-ohm load for the 20 cells. The hot-side temperatures, which are underlined in this table, are estimated from either the cold side temperature or the Variac setting. All the hot-side temperatures could not be obtained directly because the thermocouples had been destroyed by electrolyte which leaked to them through the graphite. Due to a powerstat failure, Cell Nos. 11 through 15, experienced a 100°C temperature drop after 8 hours of operation. As can be seen from the data in Table 1, Cell No. 6 had the highest voltage on open circuit and a 50-ohm load. This cell had an open-circuit voltage of 0.27 v and 0.205 v on 50-ohm load, which corresponds to a current density of 0.795 ma/sq cm at a hot-side temperature of approximately 700°C. This cell was sealed with No. 7 Sauereisen cement. Cell Nos. 1, 11, and 16, which were also coated with No. 7 Sauereisen cement, were, in general, above average. After 8 hours of operation, iodine vapors were observed escaping from the cells sealed with Nos. 8 and 31 Sauereisen cement.

Table 21 shows the load characteristics for the best cell with each sealing agent tested. Again, the data indicate Cement No. 7 to be the best sealing agent.

Table 22 gives voltage and current density data for Cell No. 6 for 48 hours. The test was shut down after 48 hours.

Table 23 gives the open-circuit voltages for all cells at shutdown. No hot-side temperatures are recorded in this table, because all of the hot-side thermocouples had been destroyed. The destruction of the thermocouples could have been caused by corrosion from electrolyte absorbed in the graphite. The data again indicate No. 7 Sauereisen to be the best sealing agent.

Inspection of the cells at the termination of the test showed that the silicate glaze on all cells had blistered. The structural integrity of the cells decreased with increased operating temperature. In the cells operating at the higher temperatures (approximately 700 to 750°C), the anodes had completely disintegrated. The cathodes of these cells had been reduced to a granular mass. This loss of graphite was due to air oxidation, and could be eliminated by making tests in a vacuum or inert atmosphere, as shown in the experiment with cells Nos. 1 and 2. However, the cathodes of cells sealed with No. 7 appeared to be more intact. Of the cells operating at lower temperatures, those sealed with No. 7 cement were

more structurally sound. All of the Sauereisen cements had become embrittled by heating. Of the Sauereisens tested, cement No. 7 showed the best sealing properties over the temperature range of the test.

2. Cells Bonded with Sauereisen Cement No. 7 and Encapsulated with Rokide "A" and Pyro-Chrome Paint

Through association with the Structural Materials Division of Aerojet at Azusa, several new sealings were suggested that could be employed using the encapsulation technique of construction. Several of these materials were tested in conjunction with Sauereisen No. 7 as sealing agents. These materials were tested in the hope of obtaining a more impervious seal than could be obtained with Sauereisen alone. The materials tested were Rokide "A" and Pyro-Chrome paint

a. Encapsulation With Rokide "A"

Cell Nos. 59, 60, and 61 were sealed with Sauereisen Cement No. 7 and Rokide "A" (alumina-based material manufactured by Metallizing Corporation of America). Graphite electrodes and Electrolyte No. 14 were used. The cells were tested in air. The graphite used for electrodes in Cell Nos. 59 and 60 was 18J grade made by the National Carbon Co. These electrodes measured 1 1/2 x 1 1/2 x 7/16 in. The graphite electrodes in Cell No. 61 were of spectrographic grade (U-120) manufactured by the United Carbon Products Co. The electrodes used in this cell measured 1 1/2 x 1 1/2 x 1/8 in. Fiberfrax pads measuring 1 x 1 x 1/4 in. were saturated with Electrolyte No. 14 and stored in a 150°C oven until incorporation in a cell. In the fabrication of Cells 59, 60 and 61, the Fiberfrax pad was sandwiched between two graphite electrodes and the space between the electrodes at the edges, sealed with Sauereisen Cement No. 7. After preliminary sealing, nickel electrical leads and thermocouples were placed in holes drilled in the edges of the electrodes. The thermocouples were coated with "N" type silicate prior to insertion in the electrodes. The cells were then placed in a 150°C oven for several hours to help set the Sauereisen and expel any moisture absorbed by the graphite during fabrication. The cells were cooled in a dessicator over Drierite. Rokide "A" was applied by flame spraying techniques. Since Rokide "A" is a white material and could act as a heat rejector, a coating of high-temperature, cobalt-based paint

was applied over the Rokide. The cobalt-based paint was compounded by the Structural Materials Division of Aerojet. This paint was dark blue in color, thus reducing the heat rejection.

After the cells had been encapsulated with Rokide and painted with the cobalt paint, it was noted that the areas near the Sauereisen seals were darker blue than the rest of the cell's area. It was postulated that there may have been leakage of some electrolyte through the Sauereisen seal during the Rokide application, as it was estimated the cells reached an approximate temperature of 450°C during this process. The three cells were heated by radiation, using the same type heat source described in Sect. V, F, 1. The switching arrangement used to monitor the voltage and temperature was also the same. The material of construction data are recorded in Table 24. Tables 25, 26, and 27 give the open-circuit and load characteristics of these cells.

These cells were operated for 230 hours at a maximum temperature of 500°C . Voltage measurements on various loads were made several times during this period. The cells were allowed to cool to room temperature after 7 hours of operation and were reheated after 64 hours. Inspection of the cells before restarting showed that the temperature cycle did not cause cracking of the Rokide. After the 64-hour shutdown, the cells operated an additional 223 hours at 500°C before the test was terminated. The current densities reported in the tables are based on the original effective electrode area. Termination of this experiment was caused by loss of electrolyte through the sealing material. Destructive inspection of these cells showed that the anodes (hot side) had been almost completely consumed by oxidation even at the low operating temperature (500°C). Both types of graphite (U-120 and 18 J) were consumed by oxidation. The current densities and voltages recorded in the tables are low because of the low operating temperature. Also, it should be pointed out that the current densities reported are based on the original effective electrode area, and since there was a continual loss of electrode area with time due to oxidation, the values reported are much lower than the actual values. This difference between reported and actual values would increase with time. The actual anode current densities at the finish were about 6.8 ma/sq cm.

b. Encapsulation with Pyro-Chrome Paint

Cell Nos. 62 through 71 were sealed with Sauereisen Cement No. 7 and Pyro-Chrome, a chromium-based, high temperature paint manufactured by the Preferred Utilities Manufacturing Corp. Graphite electrodes and Electrolyte No. 14 were used. The cells were tested in air. The graphite used was spectrographic grade (U-120) and measured $1\frac{1}{2} \times 1\frac{1}{2} \times \frac{1}{8}$ in. The Fiberfrax pads saturated with electrolyte measured $1 \times 1 \times \frac{1}{4}$ in. The method of fabrication of these cells was essentially the same as that described for Cell Nos. 59, 60, and 61, the only difference being the final seal. It was made by the brush application of the Pyro-Chrome paint instead of Rokide "A."

These cells were heated by radiant heat. Cell Nos. 62, 63, 67, 70, and 71 were tested at a constant load of 10 ohms. Cell Nos. 64, 65, 66, 68, and 69 were tested at a constant load of 50 ohms. Cell Nos. 62 through 66 were held to a maximum temperature of 600°C , while Cell Nos. 67 through 71 were held to a maximum temperature of about 500°C . After 6.25 hours of operation and a maximum temperature of 355°C the cells were shut down for the weekend. Inspection of the cells before restarting showed no cracking due to the temperature cycle caused by the shutdown. The test was terminated after 54.5 hours because of loss of electrolyte through the sealing agent. The material of construction data are recorded in Table 24. Tables 28 and 29 give the voltage and current-density data for these cells.

The current-density data presented in Tables 28 and 29, as before, are based on the original effective electrode area. Destructive inspection of the cells showed almost complete consumption of the graphite anodes (hot side) due to oxidation. The current densities reported in the tables are low because of the low operating temperatures. The difference between the actual current densities and reported current densities as mentioned for Cell Nos. 59, 60, and 61 become greater with time because of loss of effective electrode area due to oxidation. The actual current densities at the finish were about 15 ma/sq cm.

3. Discussion

Evaluation of ceramic-type sealing showed that of the Sauereisen tested, Cement No. 7 was the best. Rokide "A" used in conjunction with Sauereisen Cement No. 7 as a sealing agent was inferior to the Sauereisen alone. The application of Rokide by flame-spray technique causes too great a rise in temperature of the cell, resulting in the electrolyte bleeding through the graphite. It is also possible that some loss of electrolyte occurred during the period of Rokide application. This bleeding-through of the electrolyte caused poor adhesion between graphite and Rokide. Although there was evidence that the electrolyte bled through the graphite and Rokide, as shown by the dark blue areas of the cobalt paint used as an additional seal, these cells had an operating life of 230 hours. The cells using Pyro-Chrome paint in conjunction with Sauereisen Cement No. 7 as the sealing agent had a 55-hour operating life. It should be pointed out the shorter operating life of these cells (as compared with the Rokide-sealed cells) was because the latter cells were operated at a lower temperature.

G. FABRICATION OF MODEL BATTERY FOR DELIVERY TO USASRDL

Although cells encapsulated with Rokide "A" had a longer operating life than cells encapsulated with Sauereisen alone or Pyro-Chrome paint, it was decided to construct a model battery using the Pyro-Chrome paint as the encapsulating sealing agent. The reason for choosing Pyro-Chrome was because it was believed the difference in operating life was a function of the operating temperature. The shorter life of the Pyro-Chrome encapsulated cells is attributed to their higher operating temperature. Also, it was felt that the poor adhesion between graphite and Rokide "A" in places where the electrolyte had bled through the graphite might increase with time.

A twelve-cell battery was constructed with each cell being sealed in the manner described in Section IV,F,2,b of this report. The cells were connected in series in three rows of four cells each. The battery was encased in a Lucite packing case for shipment. Because it was known that the seal was porous to some degree, packages of drying agent were sealed in a Lucite container with the battery. The battery should be kept in the dry state until testing. If exposed

to air, the hygroscopic characteristic of the electrolyte will absorb moisture, causing partial or complete damage to the battery. Again, because of the porosity of the seal, the battery should be tested in an inert atmosphere so that oxidation of graphite will not occur. If tested in air, the loss of graphite due to oxidation will cause loss of contact between graphite and the electrolyte-impregnated Fiberfrax. If tested, it is recommended that the operating temperature be maintained between 500 to 600°C to prolong cell life. At higher operating temperatures, loss of electrolyte and bismuth triiodide through the porous sealing agent will be greatly increased, causing a shorter operating life.

H. EVALUATION OF MISCELLANEOUS SEALING TECHNIQUES

Prior to the construction of the battery, a cell was constructed using a unique method for making the graphite that is used for the electrodes impervious. It is known that some forms of silicon carbide on graphite produces a impervious coating.

1. Construction

Cell No. 72, constructed using graphite (U-120) coated on one side with silicon carbide and Sauereisen Cement No. 7 as the sealing agent, operated for 51 hours in air. This cell operated at a maximum current density of 8.0 ma/sq cm on a 10-ohm load at 0.25 v, with a hot-side (anode) temperature of 750°C.

The U-120-grade graphite electrodes were each coated on one side with silicon carbide by placing the side to be coated in contact with spectral-grade silicon powder, and heating in an inert atmosphere oven at 1500°F for 15 min. Fiberfrax impregnated with electrolyte was placed between the coated electrodes, and the space between the electrodes around the edges was sealed with Sauereisen No. 7 Cement. The uncoated side of each electrode was in contact with the Fiberfrax. The Sauereisen cement was glazed with a coat of "N" type sodium silicate.

2. Data

The current density and voltage data for this cell are recorded in Table 30. This cell operated at a current density of 8.0 ma/sq cm (based on the

- original effective electrode area) on a 10-ohm load at 0.25 v with a temperature of 750°C. The cell reached a maximum temperature of 795°C. It operated for 51 hours. Destructive inspection of the cell after test showed that the anode (hot side) had been completely consumed. The silicon carbide coating was intact. It is estimated that the anode current density reached 43 ma/sq cm midway through the test.

The silicon carbide coating was highly porous. The Minnesota Mining and Manufacturing Co. reports that coatings of the material 0.006 in. thick will adhere to graphite, are nonporous, and will withstand exposure to air at 1000°C for 12,000 hours.

I. DECOMPOSITION STUDIES WITH BISMUTH TRIIODIDE

1. Objectives

It has been postulated that these cells are regenerated by the thermal decomposition of bismuth triiodide to form iodine and bismuth. A series of tests were run to demonstrate that this process does take place, and to determine the effects of other cell components such as the electrolyte, carbon electrodes, platinum catalysts, and bismuth metal.

2. Method

An apparatus was constructed for the controlled heating of cell materials, and the collection and measurement of any iodine evolved. The cell materials are placed into a Pyrex or Vycor bulb which is then heated to the desired temperature. A very slow stream of nitrogen gas at one atmosphere pressure is passed over the heated cell materials and then through a liquid nitrogen trap. Any free iodine evolved is collected in this trap, which is then washed with potassium iodide solution. This solution is then titrated with standard sodium thiosulfate to determine the amount of free iodine evolved from the heated cell materials. The electrolyte salts and iodine used in formulating the cell materials were all "C.P." or "Analyzed" grade. Bismuth triiodide was prepared in the laboratory by direct combination of the elements, and purified by resublimation in a nitrogen atmosphere.

3. Results

Dry bismuth triiodide was heated to 400, 500, 550, and 600°C. No decomposition and evolution of iodine was detected at 400°C. At 500°C, a small amount of iodine, equivalent to less than a 1% decomposition was collected. At 500 and 600°C, decomposition was substantially complete.

Electrolyte No. 12 was heated alone up to 700°C and yielded essentially no iodine. As a test of the solubility of iodine in Electrolyte No. 12, iodine was mixed in the electrolyte and the mixture heated to 500°C. After 25 min, the electrolyte was tested for free iodine, of which only a trace was detected. When a solution of bismuth triiodide in Electrolyte No. 12 was heated to 700°C, iodine equivalent to a 4% decomposition by weight of bismuth triiodide was collected.

In another experiment to find a possible catalyst to increase the rate of decomposition, a small amount of platinum thermally deposited from the chloride was without noticeable effect on the decomposition of the mixture of Electrolyte No. 12 and bismuth triiodide.

To test behavior of bismuth triiodide in the presence of bismuth, a solution of 1.5% bismuth triiodide in bismuth metal was heated alone to 750°C. The bismuth triiodide sublimed around 500°C, and was deposited in the relatively cool neck of the test bulb away from the heated zone. Upon further heating this bismuth triiodide decomposed. When this same solution of bismuth triiodide in bismuth metal was heated with Electrolyte No. 12, a larger proportion of the bismuth metal was not present.

J. EFFICIENCY OF WAFER CELLS

Early estimates of efficiency were made by dividing the measured cell energy output by the estimated energy supplied to the cell. Values obtained for the early dry-type models were 0.2%. This was encouraging when it was considered that a sizeable fraction of the energy supplied to the cell was not absorbed by the cell, but was radiated back into space. More optimized cells, such as the recent model shown in Figure 9, operated at efficiencies of around 12%, as estimated by the same method. This was known to be competitive with the advanced designs of the silicon solar cells being marketed. Theoretical studies of EMF and vapor pressure vs temperature are shown in Figures 19 and 20 respectively.

1. Description of Test Apparatus

A more realistic approach to efficiency measurement was made when more efficient cells were available for test. Figure 18 is a schematic diagram of the apparatus. The operation is briefly as follows: A disc cell, approximately $3/4$ in. in diameter and $1/4$ in. thick is placed on a steel block which is heated by an electric furnace. Above the cell is placed a water-cooled copper cylinder. Thermocouples are properly placed on the cell faces so that the temperatures of the two electrodes may be measured. Leads to the electrodes permit imposing a load on and measuring the voltage of the cell. Water flows through the cooling member and removes heat from the cooler face of the cell. The amount of heat removed is determined from the recorded inlet and outlet water temperatures and the rate of flow. The efficiency is estimated by dividing the energy delivered by the cell by the energy which has passed through the cell. The annular cell and water jacket are made of the same materials as the test cell and water chamber, and are used to maintain thermal conditions of the environment comparable with those of the test cell and cooler.

Measurements were made under conditions compatible with the use of water for cooling. For higher-temperature work, the thermal conductivities of cells and other components were obtained by extrapolation.

2. Efficiency Calculated From Experimental Data

Calorimetric tests made on the bismuth triiodide wafer cells provide data for estimating efficiency. The method of calculation used is to determine the thermal conductivity of the cell and use this value to determine heat flux in tests where no calorimetric measurements are available. The thermal conductivity of the graphite electrodes was used to determine the temperature drop through these parts at the heat fluxes measured. The results of this calculation showed less than 1°F drop in temperature for the electrode thickness. As a result, it was assumed that the electrolyte filler material controlled the heat flux through the cell. Also the heat rejected by the cell was about equal to the heat supplied. This is approximately true, since only a small amount of the heat energy is converted to electrical energy. An idealized fuel cell is shown in Figure 21.

a. Calorimetric Test Data

Calorimetric test data for two tests on a wafer-type cell are listed as follows:

	<u>Test X</u>	<u>Test Y</u>
Temperature, °C, hot electrode	603	596
Temperature, °C, cold electrode	207	200
Water temperature, in, °C	11	12
Water temperature, out, °C	12	17.5
Water flow, cc/min	31	7

b. Calculation of Heat Flow and Average Thermal Conductivity

(1) Test X

Calculation of Heat Flow

ΔT of water on cold side of cell = 1°C

$Q = \text{heat flow} = 1 \times 31 \text{ cc/min} = 0.031 \text{ kcal/min}$

$0.031 \text{ kcal} = 7.36 \text{ Btu/hr}$

Calculation of Average Thermal Conductivity k

$$Q = kA \frac{\Delta T}{X}$$

where

$Q = \text{heat flow}$

$k = \text{average thermal conductivity}$
between T_1 and T_2

$A = \text{Area at right angles to direction of}$
heat flow

$X = \text{distance between } T_1 \text{ and } T_2$

$$k = \frac{QX}{A\Delta T} \quad (1)$$

$$k = \frac{(7.36 \text{ Btu/hr})(0.050 \text{ in.})}{(0.785 \text{ in.}^2)(713^{\circ}\text{F})} \quad (2)$$

$$k = 0.000658 \text{ Btu/hr in. } ^{\circ}\text{F} \quad (3)$$

(2) Test Y

From the data given for Test Y, the value of k is

$$0.000820 \frac{\text{Btu}}{\text{hr. in. } ^{\circ}\text{F}} \quad (4)$$

c. Cell Operating Data

The electric power output from the cell data presented in Table 3, operating at 1744 and 869^oF for the hot and cold electrodes respectively, gave the following voltage-load data.

<u>Voltage</u> (volt)	<u>Load</u> (ohms)	<u>Power</u> (watts)
0.51	open circuit	0
0.50	100	0.0025
0.48	50	0.0046
0.46	33	0.0064
0.31	5	0.0191
0.20	2	0.0200
0.14	1	0.1960

d. Cell Efficiency Calculation

(1) Based on Calorimetric Test

$$\text{Electrolyte area} = 0.129 \text{ in.}^2$$

Heat flux based on value, k, of Test X

$$Q = \frac{(0.000658 \text{ Btu/hr in } ^{\circ}\text{F})(0.129 \text{ in.}^2)(1744^{\circ}\text{F}-869^{\circ}\text{F})}{0.050 \text{ in.}} \quad (5)$$

$$Q = 1.484 \text{ Btu/hr} = 0.435 \text{ w} \quad (6)$$

$$\text{Cell Efficiency} = \frac{0.020}{0.435} \times 100 = 4.6\% \quad (7)$$

(2) Based on Calorimetric Test Y, the cell efficiency is 3.7%.

K. REACTION MECHANISM FOR DECOMPOSITION OF BISMUTH TRIIODIDE

The postulated mechanism of reaction for the generation of electrical energy by the bismuth triiodide cycle is given below:

Decomposition Reaction



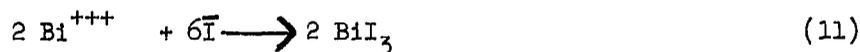
Anode Reaction



Cathode Reaction



Recombination Reaction



In a cell, on the application of heat (550°C) Reaction (8) takes place, resulting in the formation of molecular bismuth and iodine. The reaction given shows only the decomposition of bismuth triiodide to bismuth and iodine. It has been postulated that on the decomposition of bismuth triiodide some sub-iodides are formed. Whether they exist in the presence of an electrolyte (fused salts) is not known. It is reasoned that, for optimum cell operating temperatures (800 - 900°C), the steady state concentration of the sub-iodides, if any, would be negligible. After decomposition, the bismuth and iodine are separated (independently of gravity) by essentially a distillation process. At both the temperature of decomposition and the cell operating temperature, iodine (boiling point 184°C) distills away from the hot electrode (anode) and condenses on the cooler electrode

(cathode). The bismuth (boiling point, 1420°C) remains at the hot electrode. After decomposition and distillation, the following processes are involved at the electrode surfaces:

- (1) Adsorption on active electrode sites
- (2) Electron discharge and acceptance [Reaction (9) and (10)]
- (3) Desorption from electrode surfaces
- (4) Ionic migration to zone of recombination
- (5) Recombination [Reaction (11)]

As can be seen by the data presented in Table 3, an increase in cell operating temperature is accompanied by an increased electrical output.

Any increase in temperature above 600°C would have little, if any, effect on the rate of decomposition. However, the increase in electrical output observed with increased temperature could be caused by the temperature effects on any one or all of the five steps given above. Which of the five steps are affected is not yet known.

L. OPERATION IN SPACE ENVIRONMENT

The problems relating to the operation of the cell in space environment have been the most troublesome of the entire program. The Aerojet system is not expected to be damaged by many of the space conditions, such as micrometeorites and electromagnetic radiation, which are detrimental to the other energy conversion devices now being proposed. However, two conditions which will be troublesome with all thermal and chemical energy conversion systems for space use are associated with the Aerojet system. They are the high temperature required for operation, and the high vacuum present in space. Although it would be expected that the same problems would be present in other space developmental work, and solutions could be borrowed from other fields of research, the technology developed to date leaves much work still to be done.

It is desirable to operate a thermogalvanic converter at as high a temperature as possible for two reasons: first, because radiation of the waste heat from the cathode varies as the fourth power of the absolute temperature, and temperatures much below 400°C would require inconveniently large radiating surfaces; second, the greater the difference in temperature between the hot and the cold sides, the greater will be the Carnot efficiency which is possible. The hot-side temperature goal was arbitrarily set at from 900 to 1000°C , although many tests were run at much lower temperatures when it was important to establish data for extrapolation to simulated operation at the design goal.

Perhaps the most obvious question which arises in connection with the use of materials in space at high temperatures concerns their rate of evaporation. Table No. 31 (Reference 2) shows the temperature in degrees Centigrade at which sublimation will take place for the materials shown, at the rate of 0.0004 in. per year, a rate which is arbitrarily selected as permissible.

It is evident from the data in Table 31 that metals below cobalt in the list would be highly suitable (Si, Ni and Pd might be suitable in thick layers) from an evaporation standpoint when used as materials of construction for the high-temperature side of the device. The approximate losses in thickness at 1000°C for the several metals near the acceptable limit are shown in Table 32.

Metals below vanadium in Table 31, and most ceramics, have sublimation rates high enough to be out of the question as to suitability in this respect. It is from this group that most materials tried for sealing cells were selected.

An equally important problem in the development of a thermogalvanic cell for space use is the sealing of the cell against evaporation of the vital materials, such as the electrolyte, bismuth, and iodine. During many cell tests in air, the hot graphite anode was completely consumed by the oxygen of the air which penetrated the material with which the cell was sealed. It is true that the oxidation of the graphite anode by air diffusing through the coating can be eliminated by operating the cell in argon, but that is no real solution to the problem. The same pores which let the oxygen into the cell in air will let the active materials out of the cell in a vacuum. There has been some work done on the use of coatings to prevent

the oxidation of the refractory metals at elevated temperatures (Reference 3). Some of the work is pertinent to the problem of thermal cell seals. The data on matching the coefficients of thermal expansion of the coating and the base material will be different for each material examined, but some of the other published data are applicable. In this connection it should be noted that perforation of thin layers in space might take place by reason of uneven sublimation due to grain boundaries and crystal orientation.

Metallic and ceramic coatings protected molybdenum against oxidation for various lengths of time, depending on the temperature and the material used. In Table 33 are shown some typical results of tests made at temperatures around 1000°C.

In general, certain likely metals selected from Table 31, in reasonable thicknesses, do not show promise of sufficiently long operating life when used alone. Ceramic materials are promising as far as resistance to temperature cycling is concerned, but their porosity is a disadvantage. There are methods of overcoming this deficiency which have been examined only superficially because of lack of time. Future work should be directed largely along the following lines:

1. The use of multiple layers of ceramic and metals.
2. The formation of a ceramic-like coating such as SiC and Cr₂C₃ by deposition of silicon or chromium from the gaseous phase?
3. The use of high-viscosity glasses in connection with porous ceramics, to reduce porosity.

Graphite is an ideal electrode material from most standpoints. Its one drawback is its porosity. Silicon or chromium carbides formed by gaseous-phase deposition of the metal on the graphite surface are substantially nonporous. These coatings will adhere to the graphite and be resistant to damage caused by thermal shock, high temperature, and space conditions in general.

Methods have been developed for obtaining good adhesion of ceramics to graphite. Some materials which are promising are zircon (ZrO·SiO₂), silicon carbide (SiC), magnesium silicate (MgO·SiO₂), alumina (Al₂O₃), beryllium oxide (BeO), and various proprietary compounds such as certain Sauereisen cements and Rokides. Metals can be bonded to ceramics by vapor deposition, air-fired pastes, sintering, spraying, and plating.

Consideration must also be given to the thermal characteristics of multilayered coatings. If the individual layers are not bonded together, then heat transfer across the faying surfaces occurs by conduction through the thin air film separating them when operation is in air. When operation is in space then heat must be transferred across the reduced gas pressure (dependent on vapor pressure of components), between the surfaces largely by the less-efficient process of radiation. Furthermore, the conductivity, reflectivity, and transparency of the coatings must all be considered, as well as the chemical, physical, and mechanical properties.

Many coatings appear to be physically and chemically satisfactory in all respects except for porosity, and it is believed that the proper approach toward the solution of this problem has been shown. The development of the techniques of forming these coatings would be expected to result in operating lives of several thousand hours in the near future.

V. CONCLUSIONS

A. INTRODUCTION

The great importance of the development of a thermogalvanic method of converting heat into electrical energy is emphasized by the tremendous effort which has been expended in this field. Primary batteries of the classical types, as well as the more recent fuel cells, are both excessively heavy for use in remote places for extended periods of time. The use of present day storage batteries, with their limited life based on realistic deep-charge/discharge cycles, presupposes a sizable generator. The attempted adaptation of fuel cells to storage battery use, by electrolytically decomposing the end product and then storing the reactants for later use, also requires the same over-sized generator and presents the additional problems associated with developing a reliable storage battery from a fuel cell, and of developing a practical electrolysis cell for space use. Energy conversion devices other than the thermogalvanic cell require storage batteries for the storage of energy for use during nonproductive periods.

The closed-cycle, thermogalvanic cell regenerates the reactants within the system by the absorption of heat, and can store the reactants for future use. The Aerojet system has been demonstrated to be the least complicated of the many proposed. It is potentially capable of the unusually high power density of 10 w per pound, and a storage capacity comparable with present-day storage batteries.

For a better understanding of the work accomplished under the present contract, some background material is first presented in this summary, which has been taken from previously unpublished work sponsored by Aerojet.

B. BACKGROUND

An analysis was made of many chemical compounds to determine which showed the promise of being suitable for use in a closed-cycle thermogalvanic generator. The properties required have been the subject of many papers, and will not be discussed in detail here (Reference 1). The elements of the compound which is to be decomposed by heat must have physical properties sufficiently different to permit their separation. They must be capable of being recombined in a cell in such a manner that the original compound is reformed and an electric current is produced. A thermodynamic analysis of the process is presented in the appendix. Of the many compounds which appeared to show promise, bismuth triiodide was outstanding in having properties which made it especially adaptable to testing under easily obtainable laboratory conditions. At a pressure of one atmosphere, the compound was reported to decompose at 500°C . The iodine formed has a boiling point of 183°C , the bismuth a boiling point of 1470°C . It is evident that separation of the elements should be easily accomplished by distillation. The densities are also sufficiently different to permit separation by gravity.

C. AEROJET PROPRIETARY DEVELOPMENT

1. Laboratory tests demonstrated conclusively that bismuth triiodide was decomposed at 500°C into bismuth and iodine and that the elements could be separated without difficulty. Air, of course, must be excluded or the bismuth will be oxidized and lost to the regenerative cycle. Further tests demonstrated that usable voltages and current densities could be obtained in simple primary cells from the recombination of the bismuth and iodine liberated, using any of several fused salt electrolytes.

2. Of the many applications toward which the development could be directed, that of intermediate-to-large-size liquid generators was selected for the first effort in the Aerojet program. Some results of this work suggested the possibility of constructing thin wafer-type cells in which the action of gravity is not required for separation of the reactants. In its simplest form, a cell

comprises a sandwich of electrolyte, absorbed in a carrier, between two carbon plates. Figure 1 is a diagrammatic representation of such a cell. Originally, the mechanism envisioned was one of intermittent operation, in which cells would be heated on one side to decompose the bismuth triiodide and distill the iodine to the cool side, where it would condense and dissolve in the electrolyte at the cathode surface. The bismuth formed would remain on the hot surface where it would become the anode. When the whole cell was cooled to below 500°C , the reactant elements would ionize to produce an electric current, and the ion species produced would combine to regenerate the parent compound. The cell could be stored with its elements separated, especially if maintained below a certain critical temperature, until such time as its stored energy was required. Surprisingly, it was found that the cells would continue to deliver current for as long as heat was supplied to one face and removed from the other. It is the development of these wafer-type cells for use in space applications which was the object of the Signal Corps' investigation.

3. Preliminary tests have shown that many metallic iodides will operate in the manner of bismuth triiodide in the wafer-type cells. Although some voltage on light loads will be developed with most of them, possibly as the result of thermal or concentration effects, only a comparative few will operate at as high a current density as the bismuth triiodide.

Table 1 shows the voltage developed from a selected group of salts when dissolved in an iodide-free electrolyte.* It will be observed that a voltage is generated in each test when the two electrodes are held at different temperatures, and no current is drawn from the cell. If a load is applied to the cell, however, the choice of reactants is important. The voltages on the loads shown are at a minimum for the electrolyte alone and with potassium iodide added. The highest voltages shown are for the electrolyte containing bismuth triiodide, the values being about the same as those for bismuth triiodide alone, in which case it acts as its own electrolyte. Intermediate values are shown for zinc, cadmium and copper iodides. Mercurous iodide, which gave low voltages under these conditions, gave better results at lower temperatures.

Table 2 shows comparable data for a lower melting electrolyte with the anode temperature again around 900°C. In this case, the combination of bismuth triiodide and the electrolyte is superior to either of them alone. Zinc iodide and gold chloride are inferior, platinum chloride the same, and palladium chloride superior to the bismuth triiodide.

To illustrate the effect of more suitable temperatures, some of the reactants shown in Table 2 are also shown for operation at anode temperatures around 400°C in the same table. Under these conditions platinum chloride is the best, followed by gold chloride, then palladium chloride. Bismuth triiodide and zinc iodide are no better than the electrolyte alone. Figure 2 shows the effect of temperature on power density for representative reactants, and the additive effect of certain reactants used together.

Prior to the work performed for the USASRD L under Contract No. DA 36-039 SC-87229, the wafer cells were developed to the point where a voltage of 0.20 v was obtained at a current density of 133 milliamp per sq cm of extended electrode surface (see Table 3). The life, however, was limited because the cells were operated in air, and were not properly sealed. Not only was there a rapid loss of iodine to the atmosphere, but the bismuth was oxidized, and thus was also lost to the system.

D. WORK SPONSORED BY USASRD L

The investigation for the Signal Corps under this contract was chiefly intended to demonstrate that the system would operate regeneratively, and to find a means of sealing the cell for use in a space environment.

That the cell operated regeneratively was demonstrated by the following facts:

1. When oxygen was excluded, such as by operation in an atmosphere of argon, the life of the cell was increased from a few hours to 120 hours.
2. When a control test was made, using a wafer cell from which the bismuth triiodide was omitted, the cell was virtually inoperative.
3. Iodine and bismuth triiodide were lost from the cell (cf. Item 1) during operation. This loss accounted for the ultimate cessation of cell operation.

4. Chemical tests have demonstrated that bismuth triiodide decomposes when heated in the absence of oxygen, either in the pure, dry state or when it is dissolved in a fused salt electrolyte or in bismuth metal. The bismuth and iodine formed are easily separated.

5. Bismuth and iodine combine in a conventional primary battery to form bismuth triiodide and produce an electric current.

The fact of regeneration having been established, the remainder of the time available was devoted to the much more formidable problem of enclosing the cell in an envelope to adapt it for operation in space. Because of the potentially tremendous advantages of the wafer system over competitive types, which would require pumps, separators, means for interrupting the metal and electrolyte streams when cells are connected in series, and other auxiliary equipment, the effort was directed exclusively to the sealing of individual wafer cells. The possibility of sealing a series-connected battery within a single transparent envelope (such as a glass bubble) and radiating the heat through the glass has not been pursued because simplicity and portability would be lost, though perhaps not to the extent that they are lost in the batteries which require complex auxiliary equipment. For similar reasons, the liquid type of cyclical operation mentioned in Section IV,C,2 was not pursued during this program.

In a program comprising the examination of methods and materials of construction, 13 different designs, 21 materials, and 7 assembly techniques were tested. The most promising cells were of the simplest design, that shown in Figure 3. This cell was made by coating graphite electrodes on one side with a non-porous ceramic material such as silicon carbide or Rokide "C." To improve heat radiation, the light-colored Rokide was coated with a blue cobalt-based paint. The edges of the cell were sealed with a ceramic cement of limited porosity. Leads to the two graphite electrodes penetrated the seals. Using such a construction, the lives of the cells when operated in air have been increased from a few hours to 230 hours. Failure of the cells at that time appeared to be due to the presence of pores in the coatings; the pores resulted from difficulties encountered in coating procedures.

VI. OVERALL CONCLUSIONS

The design goals set forth in the proposal on the subject contract for the operation of a regenerative thermogalvanic cell utilizing bismuth triiodide as the thermally regenerative component were to develop a cell having a current density of 111 ma/sq cm at 0.3 v, at a temperature of 900°C, and having the capability of intermittent operation for 1000 hours. An unsealed cell (data presented in Table 3) operated in air with graphite electrodes and Electrolyte No. 14 developed a current density of 111 ma/sq cm at 0.3 v with a hot-side temperature of 900°C. Sealed cells (Nos. 59, 60, and 61) operated in air at a hot side temperature of 500°C (not optimum temperature) for 230 hours. Thus, the current density and voltage goals, and a cell life equal to 23% of the design goal, have been attained. In addition to the original design goals, cell operation in the absence of oxygen (data presented in Tables 4, 5, and 6 for original argon test, and Tables 16, 17, 18, and 19 for Cells Nos. 30, 32, 33, 34, and 35), and the $\text{BiI}_3 \rightleftharpoons \text{Bi} + 1.5 \text{I}_2$ regenerative cycle have been demonstrated. Thus, the work under the subject contract has accomplished (1) the design goal for current density and voltage have been attained, (2) an operation life of 23% of the design goal has been attained, (3) cell operation in the absence of oxygen has been proven, and (4) the regenerative cycle for bismuth triiodide has been demonstrated.

VII. RECOMMENDATIONS

An operating life of 230 hours was achieved; the limiting factor was the porosity of the seals used in cell construction. Pores in the seal shorten cell life in two ways: (a) the loss of electrolyte and iodine from the cell by evaporation and seepage, and (b) the oxidation of the graphite anode and bismuth metal by the oxygen which penetrates into the cell from surrounding air.

The losses of the latter can be eliminated by operation of the cell in an inert atmosphere, but such operation will not correct the damage of the former. The oxidation of graphite causes lack of contact within the cell, and the oxidation of bismuth removes it from the regenerative cycle.

The pores are often characteristic of the methods of application rather than the material used. By perfecting methods of application of various ceramics, enamels, and other compounds it is expected that a life of several thousand hours will be obtained.

It is recommended that the program for the development of a regenerative, thermogalvanic cell utilizing bismuth triiodide as the regenerative component be continued and directed toward the screening and selection of suitable new impervious sealing materials for cell fabrication and into their methods of application. The program objectives would be the selection of an impervious sealing agent which would be compatible with the electrochemical system, and would be stable both chemically and structurally at cell operating temperatures. One such material recently reported in the trade literature which would meet the above sealing-agent requirement is impervious silicon carbide coating on graphite. The Texas Instruments Company markets a silicon carbide coating on graphite which is impervious, and resists thermal shock, abrasion, oxidation, and mineral acids at all concentrations and temperatures. It has a thermal conductivity of 70 Btu (hr)(sq ft) ($^{\circ}$ F/ft). Impervious silicon carbide and molybdenum silicate are also offered by other companies.

VIII. IDENTIFICATION OF PERSONNEL

A. LEVEL OF EFFORT

	<u>Hours</u>
W. P. Knight	108
H. E. Lawson	392
R. F. Fogle	2016
L. W. Rarogiewicz	<u>166</u>
Total	2682

B. PERSONNEL

The project cognizance was assigned to Department 311, W. P. Knight, Department Head. Dr. S. D. Rosenberg, Senior Chemist, Department 311, served this project as an advisor and administrator. Mr. H. E. Lawson, Technical Specialist, Department 311, was assigned the overall responsibility for the project. Mr. R. F. Fogle, Research Chemist, Department 311, was assigned the overall responsibility for the laboratory direction of the project. Mr. L. W. Rarogiewicz, Research Chemist, Department 311, was given the task of the investigation of the decomposition of bismuth triiodide. Below are listed the work histories for Lawson, Fogle, and Rarogiewicz.

H. E. Lawson - Technical Specialist, Chemical Engineering Department

Education:

BS 1927 - Tufts College, Chemistry

Work History:

1955 to date - Aerojet-General Corporation

1949 to 1955 - Self-employed, battery manufacture

1945 to 1949 - Zenith Radio Corporation, Director of Battery Division

1941 to 1945 - Carnegie Institution of Washington, Department of Terrestrial Magnetism, John Hopkins University, Applied Physics Laboratory. Research Chemist on proximity fuse battery development.

1939 to 1941 - C. F. Burgess Laboratories, Inc., Vice President, Research

1931 to 1939 - Burgess Battery Company, Chief, Engineering and Research

1927 to 1931 - Union Carbide & Carbon Research Laboratories, Research Chemist.

Mr. Lawson received the Naval Ordnance Development Award in 1945 and the Army-Navy Certificate of Appreciation in 1949 for his work on primary batteries. He has been cognizant engineer in charge of Aerojet's Fuel Cell development, and is Project Manager on this program. Mr. Lawson holds twelve patents in the battery field.

R. F. Fogle - Research Chemist, Chemical Engineering DepartmentEducation:

BS 1950 - Iowa State College, Chemistry
MS 1954 - University of Washington, Physical Chemistry

Work History:

1961 to date - Aerojet-General Corporation
1954 to 1961 - Olin Mathieson Chemical Corporation
1950 to 1952 - Moorman Manufacturing Company

At Moorman Manufacturing Company, Mr. Fogle was in charge of the protein quality control laboratory. Mr. Fogle's work at Olin Mathieson included work on high-energy fuels, and in the electrochemical department. For four years he was associated with the development of electrolytic mercury cells for the production of caustic and chlorine. This work included cell and anode design, and investigation of anode material. He then served as technical assistant on start-up operation of a mercury cell plant. He was the project engineer for a program investigating the electrodeposition of precious metal on various base metals.

L. W. Rarogiewicz - Research Chemist, Chemical Engineering DepartmentEducation:

BS 1957 - University of Michigan, Chemistry

Work History:

1961 to date - Aerojet-General Corporation
1953 to 1956 - Truscon Laboratories
1952 (summer hire) - Jones-Dabney Division of Devoe & Reynolds Corporation

At Truscon Laboratories and Jones-Dabney, Mr. Rarogiewicz was employed in the formulation, small-scale manufacture, application, and testing of various types of automotive, domestic, industrial, and specialized chemical resistant coatings.

Since joining Aerojet-General Corporation, Mr. Rarogiewicz has been engaged in alloy investigations and company-sponsored research on the thermal decomposition of chemical compounds. The latter studies were part of research conducted under the regenerative thermogalvanic battery program.

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TABLE 1

EXAMINATION OF POTENTIAL THERMALLY REGENERATIVE
 REAGENTS IN ELECTROLYTE NO. 11 *
 (Anode Temperature about 900°C)

<u>Test No.</u>	<u>Reagent</u>	<u>Voltage Obtained at 900°F Under Load</u>		
		<u>No Load</u>	<u>33 Ohms</u>	<u>10 Ohms</u>
1	Electrolyte No. 11	0.41	0.00	0.00
2	BiI ₃	0.25	0.22	0.12
3	BiI ₃ in electrolyte	0.50	0.23	0.10
4	ZnI ₂ in electrolyte	0.59	0.11	0.03
5	CdI ₂ in electrolyte	0.57	0.12	0.04
6	CuI in electrolyte	0.66	0.12	0.04
7	HgI in electrolyte	0.64	0.06	0.02
8	KI in electrolyte	0.56	0.01	0.00

 * An Aerojet proprietary electrolyte.

TABLE 2

EXAMINATION OF POTENTIAL THERMALLY REGENERATIVE REAGENTS IN ELECTROLYTE NO. 12*
(Anode Temperature as Noted)

Test No.		Voltage Obtained at 900°C Under Load			Voltage Obtained at 400°C Under Load		
		No Load	33 Ohms	10 Ohms	No Load	33 Ohms	10 Ohms
1 & 2	Electrolyte No. 12	0.50	0.04	0.015	0.16	0.04	0.01
3	BiI ₃ alone	0.25	0.22	0.12	-	-	-
4 & 5	BiI ₃ in electrolyte	0.49	0.40	0.22	0.14	0.06	0.02
6 & 7	ZnI ₂ in electrolyte	0.55	0.30	0.15	0.12	0.03	0.01
8 & 9	AuCl in electrolyte	0.44	0.31	0.16	0.33	0.16	0.07
10 & 11	PtCl ₂ in electrolyte	0.67	0.40	0.20	0.44	0.29	0.14
12 & 13	PdCl ₂ in electrolyte	0.55	0.49	0.38	0.32	0.13	0.05

* An Aerojet proprietary electrolyte.

TABLE 3

EVALUATION OF WAFER-TYPE CELL UTILIZING ELECTROLYTE NO. 14* + BISMUTH TRIIODIDE
(Test No. 12/22/60-3; 22 Dec. 1960)

Elapsed Time, Min	Temperature, °C		LOAD (OHMS)												Internal Resistance (ohms)		
	Anode	Cathode	I - VOLTAGE OF LOAD (VOLTS) ^c														
	0C		680	500	330	200	100	50	33	20	15	10	5	2	1	0.5	0.33
0	0.00	75						0.01	0.13	0.14	0.08	0.05	0.03	0.01			
10	0.12	90	0.09	0.08	0.07	0.04	0.02	0.16	0.22	0.19	0.18	0.14	0.09	0.04	0.02	0.01	0.01
20	0.20	115	0.20	0.20	0.20	0.19	0.18	0.23	0.22	0.19	0.18	0.14	0.09	0.04	0.02	0.01	0.01
30	0.25	140	0.25	0.25	0.25	0.24	0.24	0.23	0.22	0.19	0.18	0.14	0.09	0.04	0.02	0.01	0.01
40	0.20	165	0.20	0.20	0.20	0.20	0.19	0.18	0.17	0.14	0.12	0.09	0.06	0.03	0.02	0.01	0.01
60	0.22	200	0.22	0.22	0.22	0.22	0.21	0.20	0.19	0.16	0.15	0.13	0.09	0.05	0.03	0.02	0.02
70	0.36	235	0.36	0.35	0.35	0.35	0.34	0.31	0.29	0.25	0.24	0.20	0.14	0.08	0.05	0.03	0.02
80	0.32	300	0.32	0.32	0.32	0.31	0.30	0.29	0.27	0.25	0.24	0.21	0.17	0.10	0.06	0.04	0.03
95	0.42	360	0.42	0.42	0.41	0.41	0.40	0.39	0.37	0.35	0.33	0.29	0.22	0.13	0.09	0.05	0.04
105	0.47	420	0.47	0.47	0.47	0.46	0.45	0.44	0.42	0.38	0.36	0.32	0.25	0.14	0.10	0.05	0.04
110	0.51	430	0.51	0.50	0.50	0.49	0.48	0.46	0.44	0.38	0.36	0.31	0.28	0.18	0.12	0.08	0.07
123	0.51	465	0.51	0.51	0.51	0.50	0.50	0.48	0.46	0.42	0.41	0.37	0.31	0.20	0.14	0.08	0.07
135	0.46	510	0.46	0.40	0.39	0.38	0.37	0.36	0.35	0.32	0.31	0.28	0.23	0.15	0.10	0.07	0.05
140	0.65	455	0.65	0.65	0.65	0.64	0.63	0.61	0.57	0.50	0.47	0.40	0.30	0.16	0.11	0.06	0.05

		II - CURRENT DENSITY (MA/CM ²) ^{***}															
		6.00	0.15	0.21	0.28	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
0	272																
10	344	0.00	0.15	0.21	0.28	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
20	420	0.39	0.53	0.67	0.81	1.27	1.60	2.40	3.20	4.80	6.14	8.90	12.7	16.0	18.7	24.0	26.6
30	492	0.49	0.67	0.81	1.01	1.60	2.40	3.20	4.80	6.85	9.33	10.6	12.0	14.0	16.0	20.0	26.7
40	534	0.39	0.53	0.89	0.89	1.47	2.60	5.34	7.67	10.7	13.3	17.3	24.0	33.3	40.0	53.4	80.7
60	642	0.43	0.59	0.93	1.41	2.34	4.54	8.28	11.7	16.7	21.3	26.6	37.3	53.3	66.6	80.0	80.7
70	700	0.71	0.93	1.41	1.89	2.07	4.00	7.75	10.9	16.7	21.3	28.0	45.4	66.6	80.0	107.0	121.0
80	780	0.63	0.85	1.29	1.66	2.74	5.33	10.8	14.9	23.3	29.3	38.7	58.7	86.6	120.0	133.0	162.0
95	852	0.82	1.12	1.66	1.90	3.07	6.00	11.7	17.0	25.3	32.0	42.6	66.0	95.3	133.0	133.0	162.0
105	904	0.92	1.25	1.90	2.06	3.26	6.40	12.3	17.8	25.3	32.0	41.4	75.8	120.0	160.0	213.0	283.0
110	916	1.00	1.34	2.02	2.06	3.33	6.66	12.8	18.6	28.0	36.4	49.2	82.4	133.0	187.0	213.0	283.0
123	952	1.00	1.36	2.06	2.06	3.33	6.66	12.8	18.6	28.0	36.4	49.2	82.4	133.0	187.0	213.0	283.0
135	992	1.04	1.57	2.54	1.57	2.54	4.93	10.4	14.1	21.3	27.5	37.3	61.3	100.0	133.0	186.0	202.0
140	944	1.27	1.73	2.62	2.62	4.27	8.40	16.3	23.0	33.3	41.6	53.3	80.0	107.0	147.0	160.0	202.0

* An Aerojet proprietary electrolyte.
 ** Internal resistance read on open circuit with 1000 cycle AC.
 c Cells were on open circuit between load check measurements.

TABLE 4

REGENERATIVE GALVANIC CELL OPERATED IN AIR
(First Test)

<u>Cell No.</u>	<u>Model</u>	<u>Max. Volts on 33 Ohms</u>	<u>Temperature, °C</u>	
			<u>Anode</u>	<u>Cathode</u>
1	A ^a	0.49	770	422
2	A	0.34	770	188
3	A	0.21	609	135
4	A	0.48	783	207
5	B ^b	0.48	673	168
6	B	0.39	661	184
7	B	0.43	716	187

^a Graphite anode and cathode

^b Nickel anode, graphite cathode

TABLE 5

REGENERATIVE GALVANIC CELL OPERATED IN ARGON
(Second Test)

<u>Hours Under Test (Cumul.)</u>	<u>Average Temp., °C</u>		<u>Voltage Obtained Under Load</u>		<u>Current Density (ma/cm²)</u>
	<u>Anode</u>	<u>Cathode</u>	<u>Open Circuit</u>	<u>50 Ohms</u>	
2	679	190	0.49	0.29	.18
18	170	39	0.0	0.0	-
46	690	190	0.62	0.35	.23
121	650	170	0.22	0.0	-

Tables 4 and 5

TABLE 6

REGENERATIVE GALVANIC CELLS OPERATED IN ARGON*
(Third Test)

Parameter	Cell Number and Type of Seal			
	1	2	3	4
	Open	Sauereisen	Astroceram + Sauereisen	Open
Quantity of bismuth triiodide	4%	4%	4%	None
Maximum voltage on 500-ohm load, volt	0.46	0.15	0.16	**
Total output, whr x 10 ⁻⁵	461.7	335.2	146.8	21.4***
Total time operated in argon, hours	81.0	77.6	173.5	-
Total time operated in static argon, hr	60.0	56.6	137.0	-
Oxygen present in static argon, ml	0.012	0.012	0.012	0.012
Time required to consume oxygen (static conditions), minutes	9.5	12.0	10.1	-
Iodine recovered in KI-trap, %	21.6	6.1	0.0	7.4
Bismuth triiodide decomposed to yield recovered iodine	22.7	6.4	0.0	-

* Using Electrolyte No. 12, graphite electrodes. Output due to oxygen (static conditions) was 3.44 milliamp minutes.

** Variable voltages of a very low order were observed intermittently for first 53 hours.

*** Approximated from intermittent outputs.

TABLE 7
CERAMIC ADHESION AND STRUCTURAL STABILITY TESTS

Material	Mounted On	Temp.	Atmosphere	Results
Sodium Silicate D	Graphite	1000°C	Air	Beaded ^a
Sodium Silicate RU	Graphite	1000°C	Air	Beaded
Sodium Silicate N	Graphite	1000°C	Air	Beaded
Sodium Silicate R	Graphite	1000°C	Air	Beaded
Sodium Silicate GD	Graphite	1000°C	Air	Beaded
Sodium Silicate G	Graphite	1000°C	Air	Beaded
Astroceram BLP (thick coating)	Graphite	1000°C	Air	Cracked
Astroceram BLP (thin coating)	Graphite	1000°C	Air	Very brittle, did not crack
Astroceram ALP	Graphite, wet ^b	150°C	Air	Good
Astroceram ALP	Graphite	150°C	Air	Good
Astroceram ALP (very thin coating)	Graphite	150°C	Air	Good
Sagger Cement	Graphite, wet	150°C	Air	Good
Sagger Cement	Graphite	150°C	Air	Good
Baymal	Graphite & Nickel	1000°C	Air	Poor, crumbled
Typersul	Graphite & Nickel	1000°C	Air	Poor, crumbled
Baymal and Typersul	Graphite & Nickel	1000°C	Air	Poor, crumbled
Sauereisen No. 29 & Silver Paint	Graphite & Nickel	1000°C	Air	Good
Astroceram BLP	Vycor	1000°C	Air	Good
Astroceram ALP	Vycor	1000°C	Air	Good

^a "Beaded" means material did not spread into an adherent film.

^b Ceramic was sandwiched between material indicated.

TABLE 8

MATERIAL OF CONSTRUCTION SUMMARY OF CELLS NO. A1 THROUGH A22

Cell No.	Cell Type	Anode	Cathode	Electrolyte	Active Agent	Sealing Agent	Insulation	Electrolyte Carrier	Environment
A1	Ceramic	Graphite	Graphite	No. 12	BiI ₃	Astroceram BLP Grade	Astroceram BLP Grade	Fiberfrax	Air
A2	Ceramic	Graphite	Graphite	No. 12	BiI ₃	Astroceram ALP Grade	Astroceram ALP Grade	Fiberfrax	Air
A3	Ceramic	Graphite	Graphite	No. 12	BiI ₃	Silver Paint	Lava	Fiberfrax	Air
A4	Ceramic	Graphite	Graphite	No. 12	BiI ₃	Silver Paint	Lava	Fiberfrax	Air
A5	Metal-Ceramic	Nickel	Graphite	No. 12	BiI ₃	Silver Paint	Lava	Fiberfrax	Air
A6	Metal-Ceramic	Nickel	Graphite	No. 12	BiI ₃	Silver Paint	Lava	Fiberfrax	Air
A7	Metal-Ceramic	Nickel	Graphite	No. 12	BiI ₃	Silver Paint Sauerreisen #7	Lava	Fiberfrax	Air
A8	Ceramic	Graphite	Graphite	No. 12	BiI ₃	Sauerreisen #7	Sauerreisen #7	Fiberfrax	Air
A9	Ceramic	Graphite	Graphite	No. 12	BiI ₃	Sauerreisen #32	Sauerreisen #32	Fiberfrax	Air
A10	Ceramic	Graphite	Graphite	No. 12	BiI ₃	Sauerreisen #32	Sauerreisen #32	Sauerreisen #29	Air
A11	Ceramic	Graphite	Graphite	No. 12	BiI ₃	Sauerreisen #7	Sauerreisen #7	Fiberfrax	Air
A12	Metal-Ceramic	Nickel	Graphite	No. 12	BiI ₃	Sauerreisen #29 and #32	Crystal "M" Paper	Fiberfrax	Air
A13	Metal-Ceramic	Nickel	Graphite	No. 12	BiI ₃	Sauerreisen #29 and #32	Crystal "M" Paper	Fiberfrax	Air
A21	Metal-Ceramic	Nickel	Molybdenum	No. 12	BiI ₃	Sauerreisen #29 plus glass wool	Sauerreisen #29 plus glass wool	Fiberfrax	Air
A22	Metal-Ceramic	Nickel	Tungsten	No. 12	BiI ₃	Sauerreisen #29 plus glass wool	Sauerreisen #29 plus glass wool	Fiberfrax	Air

TABLE 9

EVALUATION DATA FROM CELL A5

<u>Time</u> <u>(hours, cumulative)</u>	<u>Voltage</u> <u>(volt)</u>	<u>Current Density</u> <u>(ma/sq cm)</u>	<u>Temperature</u> <u>°C</u>	
			<u>Anode</u>	<u>Cathode</u>
0.5	0.01	0.002	338	158
3.0	0.43	0.100	405	187
5.0	0.42	0.100	—	—
8.0	0.40	0.096	—	—
10.0	0.37	0.089	—	—
20.0	0.30	0.072	376	176
30.0	0.25	0.060	—	—
52.0	0.15	0.036	—	—
71.0	0.05	0.012	—	—
90.0	0.02	0.005	—	—
98.0	0.30	0.072	—	241
110.0	0.08	0.020	—	—
120.0	0.15	0.036	—	—

Table 9

TABLE 10

EVALUATION DATA FROM CELL A6

<u>Time</u> <u>(hours, cumulative)</u>	<u>Voltage</u> <u>(Volt)</u>	<u>Current Density</u> <u>(ma/sq cm)</u>	<u>Temperature</u> <u>°C</u>	
			<u>Anode</u>	<u>Cathode</u>
0	0.00	0.00	75	75
1	0.05	0.04	312	95
1.5	0.20	0.16	438	115
3.0	0.13	0.10	480	172
5.0	0.05	0.04	300	98
5.5	0.10	0.08	384	122
*	--	--	--	--
71.5	0.05	0.04	314	--
72.0	0.18	0.14	452	105
72.5	0.37	0.30	605	149
73.5	0.45	0.36	701	166
74.5	0.52	0.42	616	155
78.5	0.30	0.24	652	174
84.5	0.16	0.13	--	--
91.5	0.13	0.10	--	--
96.0	0.05	0.04	--	--

* Test temporarily discontinued because of holiday weekend.

TABLE 11

EVALUATION DATA FROM CELL A7

<u>Time</u> <u>(hours, cumulative)</u>	<u>Voltage</u> <u>(volt)</u>	<u>Current density</u> <u>(ma/sq cm)</u>	<u>Temperature °C</u>	
			<u>Anode</u>	<u>Cathode</u>
0	0.00	0.00	75	75
6	0.40	0.32	466	127
*	-	-	-	-
70.0	0.00	0.00	100	75
71.0	0.26	0.21	341	117
72.0	0.40	0.32	436	144
77.0	0.39	0.31	494	155
94.0	0.26	0.21	471	145
96.0	0.35	0.28	508	152
101.0	0.24	0.19	499	161
120.0	0.10	0.08	637	115
126.0	0.10	0.08	668	111
144.0	0.02	0.02	98	30

* Battery cooled to ambient temperature for 64 hours because of weekend.

Table 11

TABLE 12

EVALUATION DATA FROM CELL A8

<u>Time</u> <u>(hours, cumulative)</u>	<u>Voltage</u> <u>(volt)</u>	<u>Current density</u> <u>(ma/sq cm)</u>	<u>Temperature</u> <u>°C</u>	
			<u>Anode</u>	<u>Cathode</u>
0	0.00	0.00	75	75
0.5	0.05	0.04	129	81
2.0	0.07	0.06	462	246
19.5	0.05	0.04	530	278
26.0	0.05	0.04	611	289
44.0	0.02	0.02	621	287
68.0	0.01	0.01	678	330
76.0	0.30	0.24	808	400
140.0	0.00	0.00	656	328
143.0	0.25	0.20	842	446
148.0	0.15	0.12	854	433
164	0.00	0.00	685	355
170	0.15	0.12	901	466
172	0.10	0.08	680	497

Table 12

TABLE 13

EVALUATION DATA FROM CELL A9

<u>Time</u> <u>(hours, cumulative)</u>	<u>Voltage</u> <u>(Volt)</u>	<u>Current density</u> <u>(ma/sq cm)</u>	<u>Temperature</u> <u>°C</u>	
			<u>Anode</u>	<u>Cathode</u>
0	0.00	0.00	75	75
8	0.09	0.07	560	324
24	0.03	0.02	580	300
27	0.04	0.03	663	329
*	--	--	--	--
146	0.02	0.02	489	259
148	0.20	0.16	769	376
151	0.15	0.12	764	371
168	0.03	0.02	--	355
194	0.01	0.01	--	381

* Test temporarily discontinued because of weekend

TABLE 14

EVALUATION DATA FROM CELL A10

<u>Time</u> <u>(hours, cumulative)</u>	<u>Voltage</u> <u>(Volt)</u>	<u>Current density</u> <u>(ma/sq cm)</u>	<u>Temperature</u> <u>°C</u>	
			<u>Anode</u>	<u>Cathode</u>
0	0.00	0.00	75	75
4	0.05	0.04	614	408
7	0.20	0.16	698	464
8	0.11	0.09	673	452
24	0.01	0.01	651	405

Tables 13 and 14

TABLE 15

DATA SUMMARY OF CELL LOAD CHARACTERISTICS

Cell No.	Hot Side Temp. °C	Operating hr (c)	Open Circuit V (d)	Open Circuit I (e)	115 Ω		50 Ω		33 Ω		20 Ω		10 Ω		5 Ω						
					V	CD	V	CD	V	CD	V	CD	V	CD	V	CD	V	CD			
23	510	1	-	-	0.175	0.26	0.136	1.88	0.41	0.130	2.44	0.51	0.11	3.59	0.65	0.100	4.43	0.71	0.09	5.59	0.81
24	500	5	-	-	0.405	0.19	0.18	0.79	0.72	0.130	0.84	0.59	0.09	0.94	0.426	0.30	1.13	0.456	0.065	1.19	0.36
25	553	28.0	0.37	-	-	-	0.15	0.66	0.50	0.110	0.66	0.37	0.07	0.73	0.26	0.06	0.85	0.26	0.04	0.79	0.16
26	666	120.0	-	-	0.35	0.26	0.11	0.68	0.24	0.07	0.65	0.15	0.05	0.73	0.13	0.03	0.52	0.04	0.02	0.62	0.04
27	630	25.5	-	-	0.25	0.19	0.09	0.56	0.16	0.07	0.65	0.15	0.05	0.69	0.10	0.04	0.83	0.11	0.05	0.93	0.09
28	594	8.0	-	-	0.32	0.24	0.21	1.21	0.88	0.18	1.69	0.98	0.13	1.94	0.78	0.11	2.28	0.81	0.08	2.49	0.64
29	574	26.0	-	-	0.345	0.26	0.17	1.05	0.55	0.15	1.22	0.51	0.09	1.32	0.36	0.08	1.53	0.38	0.06	1.71	0.30
30	740	2.0	0.53	-	-	-	0.46	2.86	4.25	0.43	4.1	5.48	0.36	5.6	6.5	0.33	6.85	7.25	0.27	8.4	7.3
31	990	2.0	0.075	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.21	6.5	4.3
32	810	2.0	0.26	-	-	-	0.22	1.37	0.90	0.21	2.12	1.27	0.19	2.87	1.71	0.17	3.54	1.81	0.14	4.35	1.96
34	850	1.5	0.305	-	-	-	0.23	1.71	1.51	0.26	2.45	2.03	0.24	3.73	2.88	0.22	4.55	3.23	0.20	6.05	3.80
35	850	1.5	0.28	-	-	-	0.25	1.55	1.25	0.24	2.21	1.57	0.22	3.34	2.31	0.20	4.15	2.60	0.19	5.43	3.06

(a) Data on open type cell taken from previous work.

(b) Cell run over weekend on 10 ohm load.

(c) Hours from first recorded voltage to load check.

(d) Volts.

(e) Current Density - mA/cm².

(f) Power - Watts X 10⁻².

TABLE 16

DATA SUMMARY OF THERMOGALVANIC CELLS

Test Date	Cell No.	Anode Material	Cathode Material	Anode Lead	Cathode Impregnated With Electrolyte	Cathode Lead	Insulator	Sealing Agent	Electrolyte Carrier	Electrolyte Used No. 12 No. 11	Environment Hr of Air Argon Operation (f)
2-8-62	23	Nickel	Graphite (c)	Nickel	No	Nickel	Sauerreisen No. 29 and glass wool	Sauerreisen No. 29 and glass wool	Fiberfrax	x	148
2-8-62	24					Nickel	Sauerreisen No. 29 and glass wool			x	128
2-13-62	25					Tungsten				x	120
2-13-62	26					Tungsten				x	166
2-19-62	27					Molybdenum				x	43
2-26-62	28				No	Molybdenum				x	24
2-28-62	29		Graphite (c)		Yes	Tungsten		Sauerreisen No. 29 and glass wool		x	48
3-7-62	30		Porous (d)					Sauerreisen No. 8 and No. 31		x	24
3-8-62	31 (a)		Porous (e)					Sauerreisen No. 8		x	24
3-12-62	32 (a)		Porous (d)							x	2
3-16-62	33		Porous (d)							x	3-5
3-19-62	34		Porous (d)							x	18
3-20-62	35 (b)	Nickel	Porous (e)	Nickel	Yes	Tungsten		Sauerreisen No. 8 and No. 31	Fiberfrax	x	2

(a) Fiberfrax pad saturated with molten electrolyte, BII, added in powered form.

(b) Bismuth metal added to cell prior to sealing and testing.

(c) National Carbon Co., Grade-18 J.

(d) National Carbon Co., Grade - Porous Carbon No. 60.

(e) National Carbon Co., Grade - Porous Carbon No. 20.

(f) Hours from first recorded voltage to shutdown.

Table 16

TABLE 17

CHEMICAL ANALYSIS* OF CELL NO. 30

	Deposit on Walls of Battery Jar <u>%</u>	Impregnated Fiberfrax from Cell <u>%</u>	Nonimpregnated Fiberfrax <u>%</u>
Al	0.03	5.2	3.4
Fe	0.014	0.08	0.02
Ni	None detected	2.1	None detected
K	None detected	2.0	None detected
Cu	Major constituent	0.002	0.01
Mg	0.02	0.03	0.06
Bi	0.54	1.2	None detected
B	Trace	0.04	Major constituent
Si	0.1	< 10	Second major constituent
Zn	1.4	> 25	None detected

* Spectrographic Analysis

TABLE 18
CURRENT DENSITY COMPARISON BETWEEN CELLS
USING ELECTROLYTE NO. 12 AND NO. 14

Cell No.	Anode Temp. °C	Voltage (volts)	Load ohms	Current Density ma/cm ²	Air Test	Argon Test	Electrolyte No. 12	Electrolyte No. 14
23	500	0.06	10	1.19	x		x	
24	500	0.04	10	0.79	x		x	
25	553	0.02	10	0.62	x		x	
26	666	0.03	10	0.93	x		x	
27	630	0.08	10	2.49	x		x	
28	-	-		-	-		x	
29	574	0.055	10	1.71	x		x	
30	740	0.27	10	8.4		x		x
31	-	0.21	10	6.5	x			
32	950	0.06	10	1.86		x		x
33	810	0.14	10	4.35		x		x
34	850	0.195	10	6.05		x		x
35	850	0.175	10	5.43		x		x

TABLE 19
OXYGEN DATA AT TIME OF ARGON SHUTOFF

Cell No.	O ₂ Present (ml)	Milliamps due to O ₂	Time to Consume O ₂ (hr)	Time Operated (hr)
30	0.189	59.7	0.03	3.0
32	↓	↓		
33			0.12	1.75
34	↓	↓	0.05	17.0
35	0.189	59.7	0.08	1.0

Tables 18 and 19

TABLE 20

DATA SUMMARY OF 20-CELL TEST

Cell No.	Sealing* Agent	Hot Side Temp. °C	Cold Side Temp. °C	Hr of** operation (hr)	Open Circuit Voltage (volt)	Voltage on 50 Ω (volt)	Current Density Ω on 50 ma/cm ²
1	7	<u>600</u> ***	-	30.75	0.175	0.12	0.465
2	8	<u>600</u>	-	30.75	0.115	0.09	0.349
3	29	591	520	12.25	0.115	0.105	0.407
4	31	620	505	11.25	0.11	0.105	0.407
5	32	493	428	7.5	0.167	0.135	0.524
6	7	<u>700</u>	-	13.75	0.27	0.205	0.795
7	8	710	630	11.25	0.145	0.130	0.504
8	29	570	475	9.5	0.145	0.130	0.504
9	31	<u>650</u>	470	9.5	0.23	0.21	0.815
10	32	750	610	11.25	0.137	0.115	0.445
11	7	<u>690</u>	-	24.0	0.212	0.155	0.600
12	8	<u>750</u>	610	12.25	0.185	0.155	0.600
13	29	<u>720</u>	650	24.0	0.18	0.135	0.524
14	31	740	-	11.25	0.192	0.170	0.659
15	32	705	540	13.75	0.155	0.110	0.426
16	7	<u>720</u>	590	13.75	0.21	0.175	0.678
17	8	700	630	9.5	0.13	0.125	0.485
18	29	<u>750</u>	640	13.75	0.10	0.097	0.376
19	31	710	610	11.25	0.175	0.150	0.581
20	32	730	600	13.75	0.11	0.08	0.310

* All cells sealed with Sauereisen Cement, numbers in table refer to cement number.

** Hours from start to voltages recorded in table.

*** Underlined temperatures are estimated from either the cold side temperature or the Variac setting.

TABLE 21

DATA SUMMARY OF LOAD CHECKS FOR CELLS OF DIFFERENT SAUREISENS IN 20 CELL TEST

Cell No.	Sealing Agent	Time (Hr)	Hot Side Temp. °C	Open Circuit Voltage (volt)	680 mA		500 mA		330 mA		200 mA		100 mA		50 mA	
					V (***)	CD (****)	V	CD	V	CD	V	CD	V	CD	V	CD
5	32	7.5	493	0.17	0.167	0.048	0.165	0.064	0.153	0.096	0.160	0.155	0.150	0.280	0.135	0.523
6	7	13.75	730	0.27	0.265	0.076	0.263	0.102	0.26	0.153	0.25	0.243	0.235	0.455	0.205	0.795
12	8	12.25	700	0.185	0.185	0.053	0.185	0.072	0.182	0.107	0.18	0.175	0.17	0.329	0.155	0.600
13	29	24.0	680	0.18	0.18	0.051	0.177	0.069	0.175	0.103	0.17	0.165	0.155	0.300	0.135	0.523
19	31	11.25	710	0.175	0.175	0.050	0.175	0.068	0.175	0.103	0.17	0.165	0.162	0.314	0.150	0.581

(*) Saureisen Cements.

(**) Hours from start to load check.

(***) V = volt under load.

(****) CD = Current Density, ma/sq cm under load.

(*****) Underlined temperatures estimated from either cold side temperature or Variac setting.

TABLE 22

DATA SUMMARY OF VOLTAGE-TIME FOR CELL No. 6 of 20 CELL TEST
(Sealing Agent Sauereisen Cement No. 7)

<u>Date</u>	<u>Time (hr)</u>	<u>Hot Side Temp. (°C)</u>	<u>Open Circuit Voltage (volt)</u>	<u>Voltage on 50Ω (volt)</u>	<u>Current Density on 50Ω (ma/cm²)</u>
4-18-62 ↓	0	19	----	----	----
	2	90	\ominus^*	----	----
	4	245	\ominus	----	----
	6	360	0.022	----	----
	8	470	0.07	----	----
	9.5	590	0.125	0.117	0.453
	10.5	680	0.13	0.105	0.406
	11.25	710	0.197	0.160	0.620
	12.25	<u>720</u> **	0.245	0.20	0.775
	13.75	<u>720</u>	0.27	0.205	0.795
	4-19-62 ↓	24.0	<u>720</u>	0.34	0.105
26.25		<u>720</u>	0.27	0.07	0.271
4-20-62 ↓	27.75	<u>720</u>	0.24	----	----
	30.75	<u>720</u>	0.195	----	----
4-20-62	48.0	<u>720</u>	----	----	----

* \ominus denotes negative value.

** Underlined temperatures are estimated from either cold side temperature or Variac setting.

TABLE 23

DATA SUMMARY OF 20-CELL TEST AFTER 48 HOURS OPERATION
 (Sauereisen Cement Sealing Agents)

<u>Date</u>	<u>Cell No.</u>	<u>Sealing Agent</u>	<u>Open Circuit Voltage (Volt)</u>
4-20-62 ↓	1	7	0.24
	2	8	0.15
	3	29	θ*
	4	31	0.03
	5	32	θ
	6	7	θ
	7	8	0.0
	8	29	θ
	9	31	0.0
	10	32	θ
	11	7	0.32
	12	8	θ
	13	29	θ
	14	31	θ
	15	32	θ
	16	7	θ
	17	8	θ
	18	29	θ
	19	31	0.01
	20	32	0.0

*
 θ denotes negative value.

TABLE 24

MATERIALS OF CONSTRUCTION OF CELLS NO. 59 THROUGH 71

<u>Cell No.</u>	<u>Anode Material</u>	<u>Cathode Material</u>	<u>Electrode Leads</u>	<u>Electrolyte</u>	<u>Sealing Agent</u>
59	Graphite	Graphite	Nickel	No. 14	Sauereisen No. 7, Rokide A***
	18J*	18J			Cobalt Paint****
60					Sauereisen No. 7, Rokide A***
					Cobalt Paint****
61	Graphite	Graphite			Sauereisen No. 7, Rokide A***
	U-120**	U-120			Cobalt Paint****
62					Sauereisen No. 7, Rokide A***
					Cobalt Paint****
63					Sauereisen No. 7, Pyro-chrome*****
64					
65					
66					
67					
68					
69					
70					
71					

* 18J Graphite-Manufactured by National Carbon Co.

** U-120 Graphite - Manufactured by United Carbon Products Co.

*** Rokide - Alumina based material manufactured by Metallizing Corp. of America.

**** Cobalt Paint - Compounded by Structural Materials Division of Aerojet.

***** Pyro-chrome - Chromium base paint manufactured by The Preferred Utilities Manufacturing Corp.

TABLE 25

OPEN CIRCUIT AND LOAD CHARACTERISTICS OF CELL NO. 59

Date	Cummu. Time (hr)	Hot Side Temp. °C	Cold Side Temp. °C	Open Circuit Voltage (volt)	300 ohms		50 ohms	
					Voltage (volt)	Current Density (ma/cm ²)	Voltage (volt)	Current Density (ma/cm ²)
5-4-62	0	20	20	0.0	--	--	--	--
	1.25	130	120	0.01	--	--	--	--
	2.25	210	190	0 ***	--	--	--	--
	4.25	285	250	0.04	--	--	--	--
	6.30	360	310	0.06	0.060	0.036	0.060	0.24
	6.88*	365	312	0.065	0.064	0.039	0.060	0.24
5-7-62	7.88	195	170	0.04	--	--	--	--
	10.38	400	320	0.08	0.080	0.049	0.079	0.32
	11.38	465	370	0.105	0.105	0.064	0.100	0.40
	12.38	495	380	0.14	0.137	0.082	0.120	0.48
	12.88	515	400	0.15	0.145	0.088	0.140	0.56
5-8-62	29.88	490	380	0.15	0.140	0.085	0.119	0.48
	30.21	490	375	0.15	0.148	0.09	0.120	0.48
	30.87	500	390	0.16	0.155	0.094	0.125	0.50
	36.37	--	400	0.18	0.173	0.105	0.138	0.55
5-9-62	42.95	--	400	0.16	0.158	0.096	0.110	0.44
5-10-62	94.37	--	--	0.22	0.195	0.117	0.105	0.42
5-16-62	230.37	--	--	0.02	0.01	0.006	0.003	0.02

* Cell was shut down at this time for 64.3 hours (weekend).
 ** Current density based on original effective electrode area.
 *** 0 denotes negative value.

Table 25

TABLE 26

OPEN CIRCUIT AND LOAD CHARACTERISTICS OF CELL NO. 60

Date	Cumulative Time (hr)	Hot Side Temp. °C	Cold Side Temp. °C	Open Circuit Voltage (volt)	330 Ohms		50 Ohms	
					Voltage (volt)	Current Density (ma/cm ²)	Voltage (volt)	Current Density (ma/cm ²)
5-4-62	0	20	20	0.0	--	--	--	--
	1.25	70	60	⊖****	--	--	--	--
	2.25	145	170	0.02	--	--	--	--
	4.25	225	190	0.04	--	--	--	--
	6.30	360	290	0.04	0.040	0.024	0.039	0.156
5-7-62	6.88*	365	295	0.04	0.040	0.024	0.039	0.156
	7.88	185	155	0.038	--	--	--	--
	10.38	400	325	0.06	0.060	0.036	0.059	0.216
	11.38	460	400	0.06	0.080	0.048	0.079	0.316
	12.38	470	360	0.11	0.108	0.065	0.101	0.405
5-8-62	12.88	485	375	0.13	0.122	0.074	0.119	0.475
	29.88	485	375	0.26	--	--	--	--
	30.21	490	380	0.38	0.08	0.048	0.02	0.080
	30.87	480	380	0.38	0.09	0.054	0.02	0.080
5-9-62	36.37	500	400	0.39	0.16	0.097	0.04	0.160
	42.95	525	380	0.33	0.15	0.091	0.04	0.160
5-10-62	94.37	-	355**	0.33	0.08	0.048	0.02	0.080
5-16-62	230.37	-	345***	0.02	0.001	0.0006	0.0	0.0

* Cell was shut down at this time for 64.3 hours (weekend).

** Temperatures are doubtful.

*** Current density based on original effective electrode area.

**** ⊖ denotes negative value.

TABLE 27

OPEN CIRCUIT AND LOAD CHARACTERISTICS OF CELL NO. 61

Date	Cumulative Time (hr)	Hot Side Temp. °C	Cold Side Temp. °C	Open Circuit Voltage (volt)	330 ohms		50 ohms	
					Voltage (volt)	Current** Density (ma/cm ²)	Voltage (volt)	Current** Density (ma/cm ²)
5-4-62 ↓	0.0	20	20	0.02	--	--	--	--
	1.25	75	70	θ***	--	--	--	--
	2.25	200	185	θ***	--	--	--	--
	4.25	260	245	0.02	--	--	--	--
	6.30	410	370	0.045	0.045	0.030	0.045	0.180
	6.88*	430	370	0.045	0.045	0.030	0.045	0.180
5-7-62 ↓	7.88	195	170	0.04	--	--	--	--
	10.38	450	435	0.06	0.060	0.036	0.060	0.240
	11.38	530	510	0.06	0.060	0.036	0.060	0.240
	12.38	540	460	0.07	0.064	0.039	0.062	0.248
5-8-62 ↓	12.88	560	475	0.07	0.070	0.042	0.068	0.272
	29.88	-	465	0.07	0.070	0.042	0.065	0.260
	30.21	-	470	0.08	0.081	0.049	0.072	0.288
	30.87	-	460	0.081	0.081	0.049	0.079	0.316
5-9-62 ↓	36.37	-	470	0.099	0.093	0.056	0.080	0.320
	42.95	-	-	0.13	0.119	0.072	0.080	0.320
5-10-62	94.37	-	-	0.17	0.152	0.092	0.095	0.380
5-16-62	230.37	-	-	0.17	0.100	0.060	0.039	0.156

* Cell was shut down at this time for 64.3 hours (weekend).

** Current density based on original effective electrode area.

*** θ denotes negative value.

TABLE 28

VOLTAGE AND CURRENT DENSITIES AT VARIOUS LOADS FOR CELL NO. 62 THROUGH 66

Date	Cumm. Time (hrs)	Hot Side Temp. (°C)	Cold Side Temp. (°C)	10 Ohms		50 Ohms		50 Ohms		10 Ohms			
				Cell #62	Cell #63	Cell #64	Cell #65	Cell #65	Cell #66				
				Current(**) Density (ma/cm ²)	Voltage (volt)								
5-18-62	6.25(*)	355	225	0.015	0.30	0.020	0.40	0.040	0.16	0.010	0.04	0.040	0.16
5-21-62	11.50	490	290	0.020	0.40	0.040	0.80	0.060	0.24	0.020	0.08	0.059	0.24
	12.00	530	320	0.020	0.40	0.050	1.00	0.070	0.28	0.020	0.08	0.060	0.24
	12.50	540	315	0.020	0.40	0.050	1.00	0.070	0.28	0.019	0.08	0.060	0.24
	13.00	570	335	0.030	0.60	0.060	1.20	0.090	0.36	0.020	0.08	0.065	0.26
	13.50	595	350	0.030	0.60	0.062	1.24	0.100	0.40	0.025	0.10	0.075	0.30
	14.50	600	350	0.030	0.60	0.065	1.30	0.100	0.40	0.039	0.16	0.072	0.29
5-22-62	30.75	—	370	0.005	0.10	0.020	0.40	0.00	0.00	0.00	0.00	0.008	0.03
	38.50	—	375	0.005	0.10	0.020	0.40	0.005	0.02	0.010	0.04	0.020	0.08
5-23-62	54.50	—	340	0.002	0.04	0.009	0.18	0.010	0.04	0.010	0.04	0.020	0.08

(*) Cells shut down at this time for 64 hours.

(**) Current density based on original effective electrode area.

TABLE 29

VOLTAGE AND CURRENT DENSITIES AT VARIOUS LOADS FOR CELL NO. 67 THROUGH 71

Date	Cumi. Time (hrs)	Hot Side Temp. (°C)	Cold Side Temp. (°C)	10 Ohms		50 Ohms		50 Ohms		10 Ohms		10 Ohms	
				Cell #67	Cell #68	Cell #69	Cell #70	Cell #71	Cell #71	Cell #71	Cell #71		
				Current(*)	Current(*)	Current(*)	Current(**)						
				Voltage Density (volt) (ma/cm ²)									
5-18-62	6.25(*)	340	220	0.02	0.40	0.020	0.08	0.025	0.10	0.01	0.20	0.010	0.20
5-21-62	11.50	445	290	0.035	0.70	0.020	0.08	0.019	0.08	0.00	0.00	0.010	0.20
	12.00	450	290	0.040	0.80	0.020	0.08	0.020	0.08	0.005	0.10	0.010	0.20
	12.50	465	300	0.040	0.80	0.020	0.08	0.020	0.08	0.010	0.20	0.010	0.20
	13.00	495	315	0.045	0.90	0.020	0.08	0.040	0.16	0.020	0.40	0.019	0.38
	13.50	500	320	0.045	0.90	0.020	0.08	0.040	0.16	0.020	0.40	0.010	0.20
	14.50	500	320	0.045	0.90	0.020	0.08	0.045	0.18	0.020	0.40	0.001	0.02
5-22-62	30.75	500	320	0.017	0.33	0.030	0.12	0.007	0.03	0.010	0.20	0.002	0.04
	38.50	510	340	0.010	0.20	0.020	0.08	0.025	0.10	0.002	0.04	0.010	0.20
5-23-62	54.50	-	330	0.010	0.20	0.000	0.00	0.010	0.04	0.002	0.04	0.005	0.10

(*) Cell shut down at this time for 64 hours.
 (**) Current density based on original effective electrode area.

TABLE 30

OPEN CIRCUIT AND LOAD CHARACTERISTICS OF SILICON CARBIDE COATED CELL

Date	Cumulative Time (hrs)	Hot Side Temp. (°C)	Cold Side Temp. (°C)	Open Circuit Voltage (volt)	330 Ohms		50 Ohms		10 Ohms	
					Voltage (volt)	Current Density (ma/cm ²)	Voltage (volt)	Current Density (ma/cm ²)	Voltage (volt)	Current Density (ma/cm ²)
4-25-62	0	18	18	0.015	0.005	0.005	—	—	—	—
	2	60	30	0.010	0.008	0.008	—	—	—	—
4-26-62	18.25	120	50	0.014	0.011	0.010	0.008	0.050	—	—
	19.25	152	65	0.022	0.019	0.018	0.013	0.083	0.003	0.096
	20.25	210	80	0.040	0.040	0.039	—	—	0.020	0.650
	23.45	380	140	0.058	0.057	0.055	0.045	0.290	0.025	0.800
4-27-62	26.00	570	—	0.170	—	—	—	—	0.150	4.800
	28.00	710	—	—	—	—	—	—	0.200	6.400
	30.00	740	—	—	—	—	—	—	0.240	7.700
	31.00	745	—	—	—	—	—	—	0.250	8.000
	32.00	750	—	—	—	—	—	—	0.250	8.000
	33.00	750	—	—	—	—	—	—	0.250	8.000
	36.00	780	—	—	—	—	—	—	0.160	5.100
	38.00	785	—	—	—	—	—	—	0.150	4.800
	40.00	785	—	—	—	—	—	—	0.130	4.200
	42.75	750	—	0.655	0.530	0.510	0.260	1.670	0.085	2.700
	43.75	770	—	0.715	0.585	0.570	0.285	1.830	0.080	2.500
49.00	795	—	—	—	—	—	—	0.140	4.500	
51.00	795	—	—	—	—	—	—	0.140	4.500	

(*) Current density based on original effective electrode area.

Table 30

TABLE 31

SUBLIMATION OF MATERIALS IN HIGH VACUUM
 Temperature ($^{\circ}\text{C}$) at which sublimation occurs
 at rate of 0.0004 in. (10^{-3} cm) per year

<u>Material</u>	<u>Temp.</u>	<u>Material</u>	<u>Temp.</u>	<u>Material</u>	<u>Temp.</u>	<u>Material</u>	<u>Temp.</u>
Cd	80	Mn	540	Si	920	Ir	1500
Se	80	Ag	590	Ni	940	Mo	1630
Zn	130	Sn	660	Pd	940	C	1680
Mg	170	Al	680	Co	960	Ta	2050
Te	180	Be	700	Ti	1070	Re	2050
Li	210	Cu	760	V	1180	W	2150
Sb	270	Au	800	Rh	1330	MgO	730
Bi	320	Ge	800	Pt	1340	ZrO ₂	1320
Pb	330	Cr	870	B	1420	BeO	1480
In	500	Fe	900	Zr	1500	ThO ₂	1600

Table 31

TABLE 32

SUBLIMATION OF METALS AT 1000°C

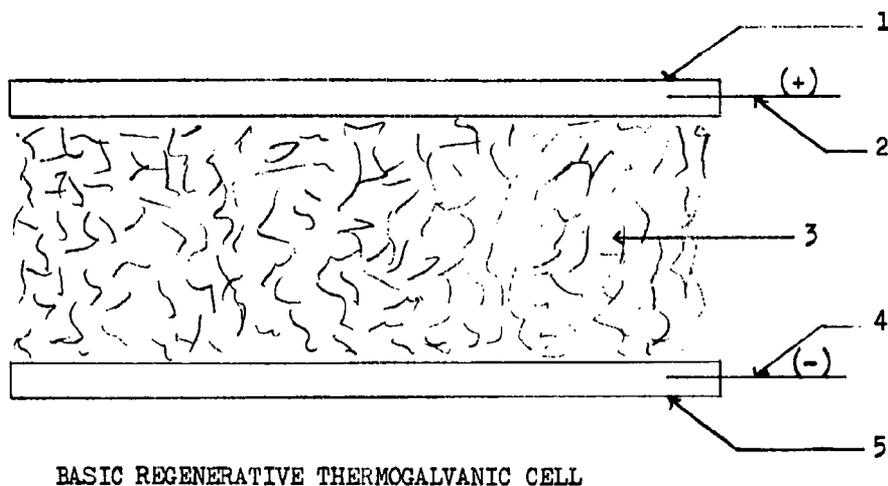
<u>Material</u>	<u>Loss, In. Per Year</u>
Fe	0.01
Si	0.006
Ni	0.004
Pd	0.0033
Co	0.0025
Ti	0.00013
V	0.000006

TABLE 33

LIFE OF COATINGS AT 1000°C

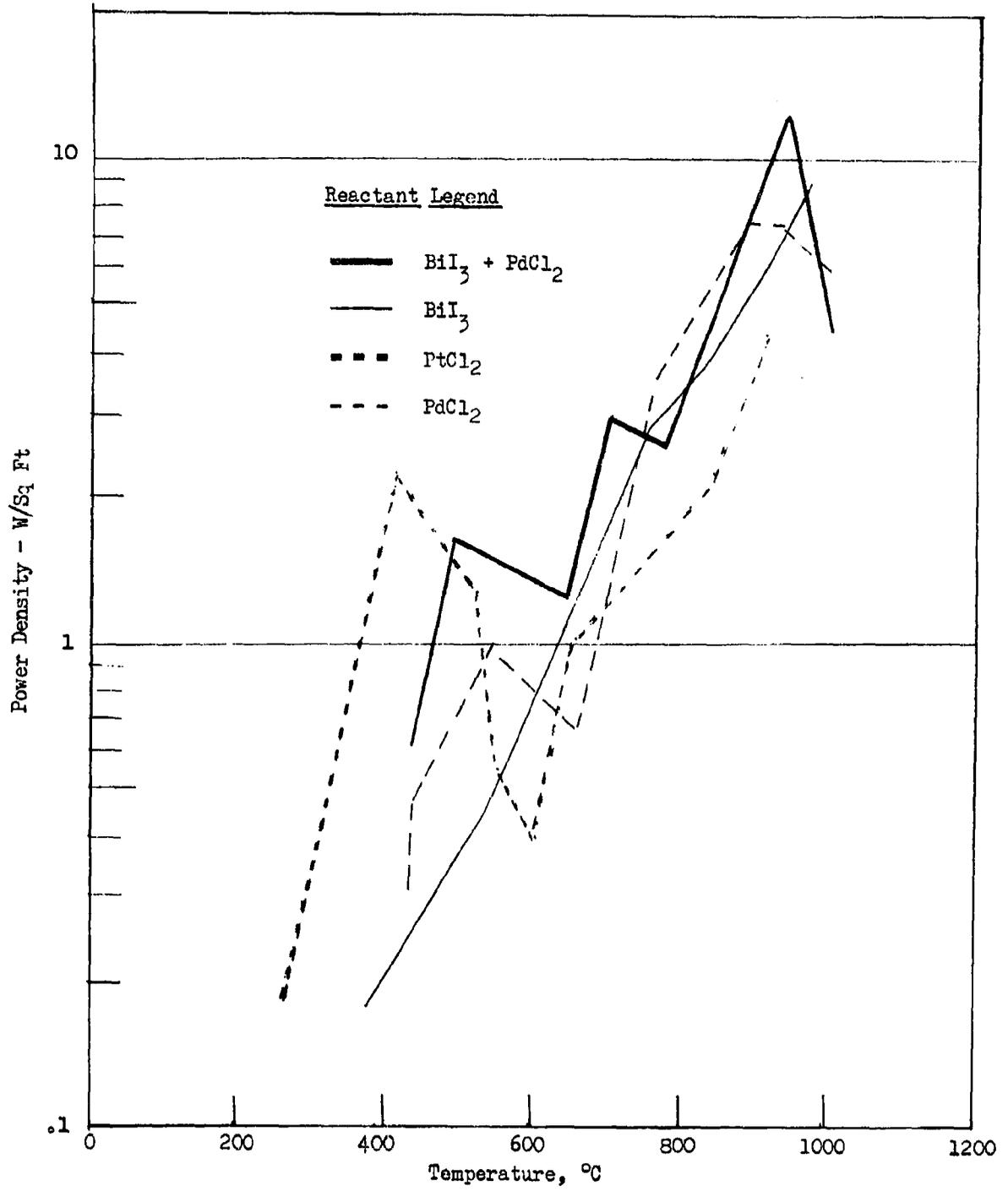
<u>Material</u>	<u>Coating Thickness (in.)</u>	<u>Coating Life (hr)</u>
Chromium	0.003	500
Iridium	0.005	0.5
Chromium	0.001	-
{ Chromium	0.001 }	740
{ Nickel	0.007 }	
Alloy (80 Ni, 20 Cr)	-	500
Molybdenum Silicide		
(a) flame spray of silicon	-	1000
(b) vapor deposition of silicon	-	3700
Platinum		
(a) by clodding	0.010 to 0.020	50
(b) with gold barrier	0.010 to 0.020	500
(c) with aluminum barrier	0.010 to 0.020	4000
Powdered Chromium in Glass Frit	-	2000

Table 33

**Cell Legend**

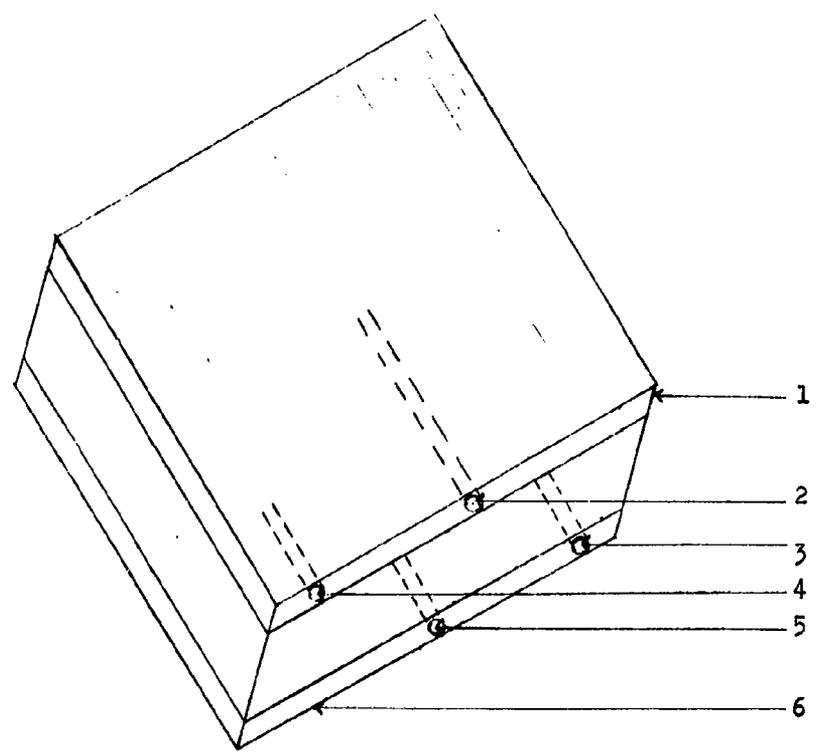
1. Cathode
2. Cathode Lead
3. Porous, non-conductive, electrolyte carrier impregnated with electrolyte
4. Anode Lead
5. Anode

Figure 1



EFFECT OF TEMPERATURE ON POWER DENSITY
 (Dry Type Thermal Energy Converter)
 (Electrolyte No. 12, 8 Ohm Load)

Figure 2

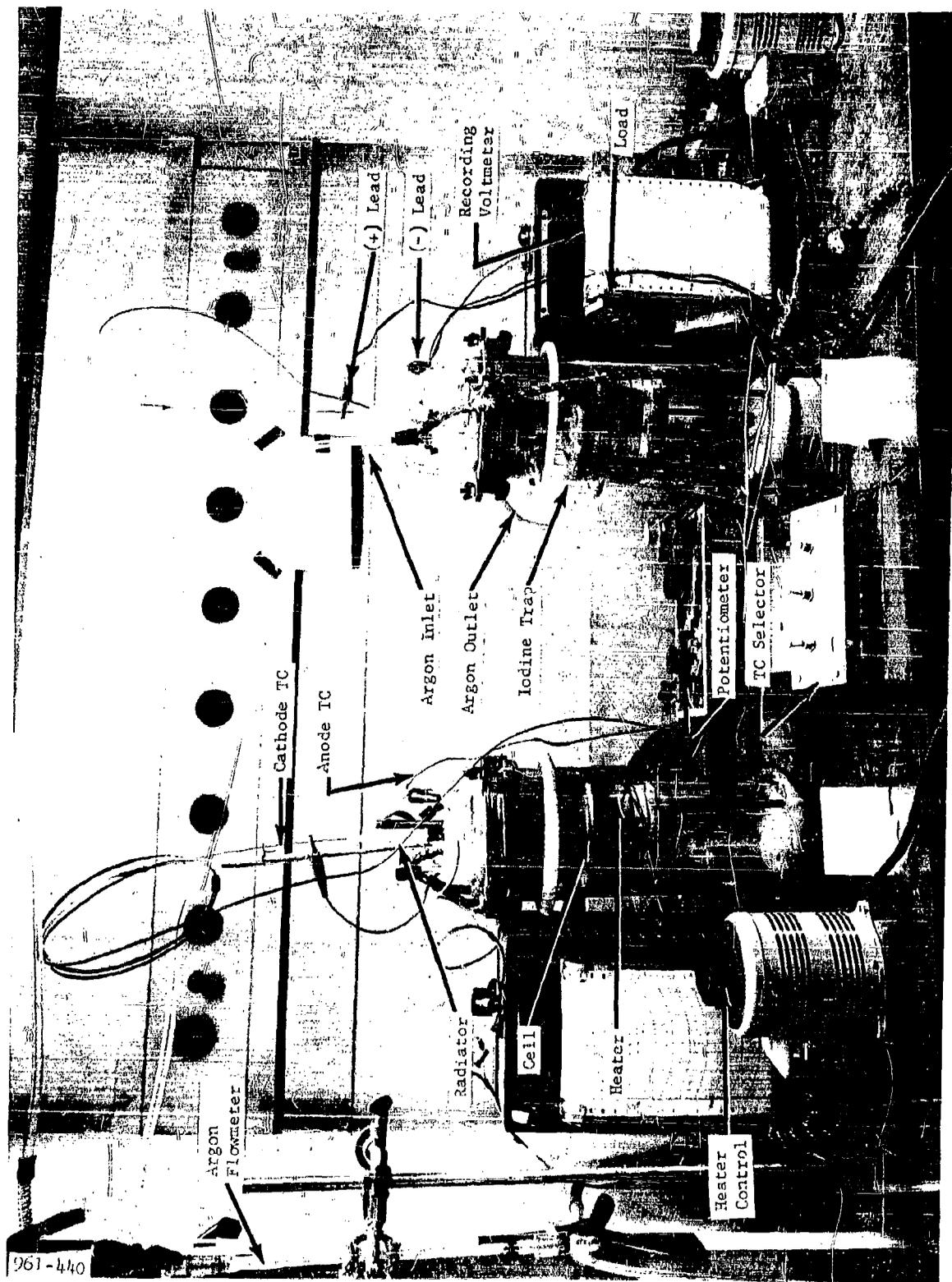


SKETCH OF CELL USED FOR 20 CELL TEST

Cell Legend

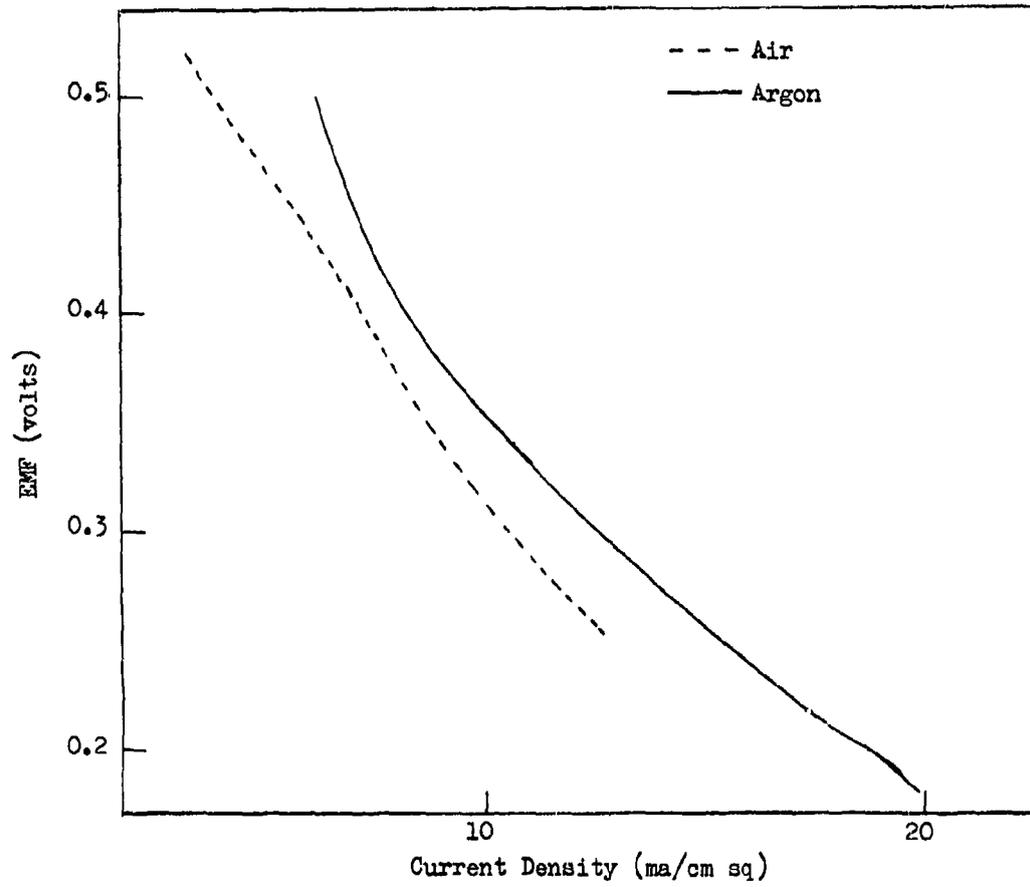
- 1. Graphite Cathode
- 2. Hole for Cathode Thermocouple
- 3. Hole for Anode Lead
- 4. Hole for Cathode Lead
- 5. Hole for Anode Thermocouple
- 6. Graphite Anode

Figure 3



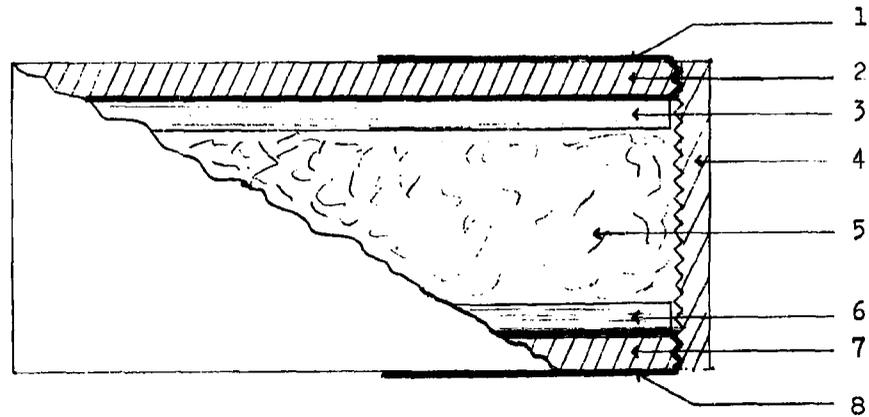
Apparatus for Testing Regenerative Cells in Argon

Figure 4



COMPARISON OF CELLS OPERATED IN ARGON AND IN AIR
(Current Density vs Voltage)

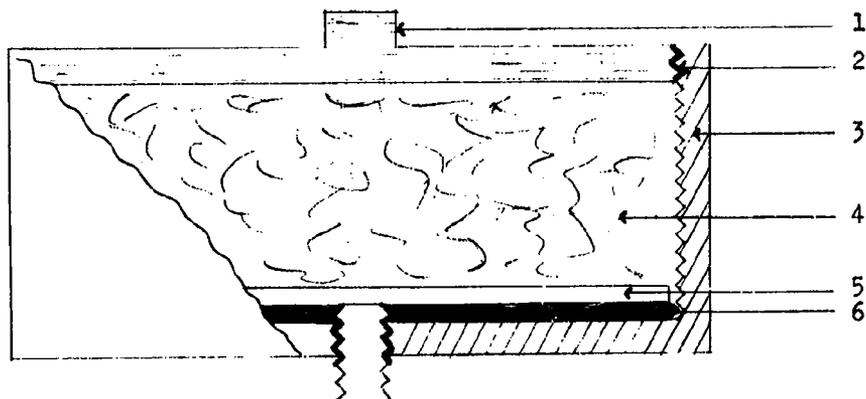
Figure 5



SKETCH OF LAVA TEST CELL A3

Cell Legend

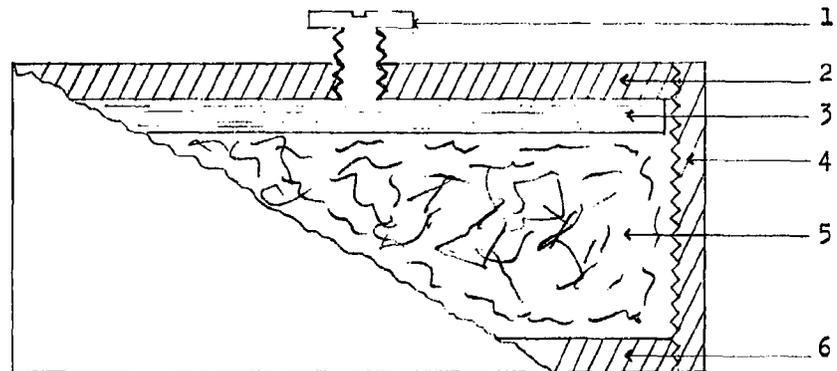
1. Gold Paint (electrical contact)
2. Lava Cathode Plug
3. Graphite Cathode
4. Lava Cell Body
5. Impregnated Fiberfrax
6. Graphite Anode
7. Lava Anode Plug
8. Gold Paint (electrical contact)



SKETCH OF TEST CELL A5

Cell Legend

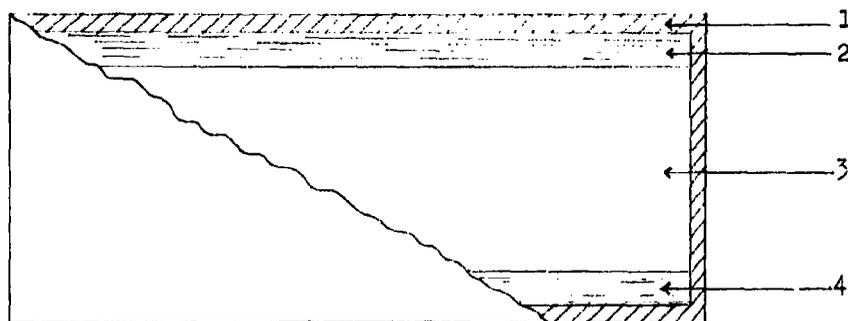
- 1. Graphite Cathode
- 2. Silver Paint (Sealing agent)
- 3. Lava Cell Body
- 4. Impregnated Fiberfrax
- 5. Nickel Anode
- 6. Silver Paint (Sealing agent)



SKETCH OF TEST CELL A6

Cell Legend

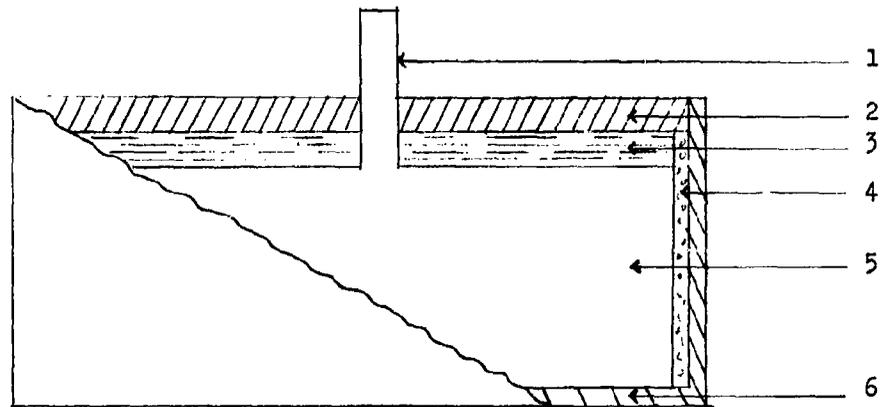
1. Nickel Screw (Electrical contact)
2. Lava Cathode Plug
3. Graphite Cathode
4. Lava Cell Body
5. Impregnated Fiberfrax
6. Nickel Anode and Plug



SKETCH OF TEST CELL AS

Cell Legend

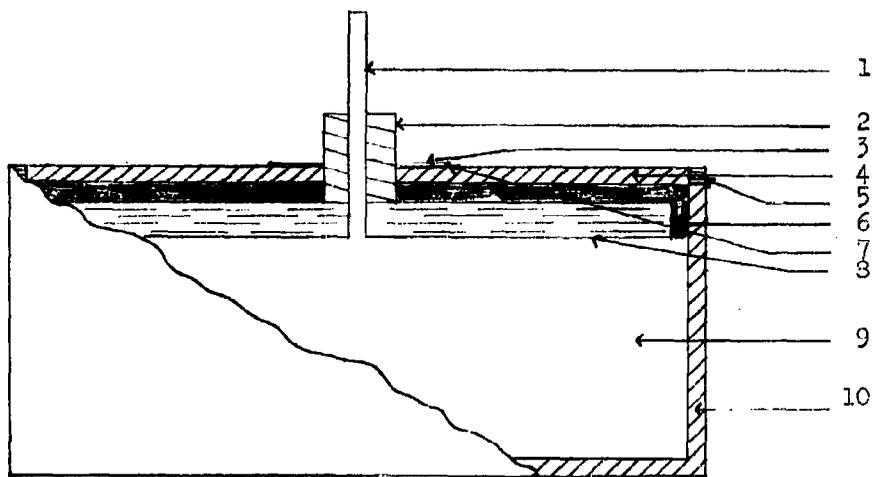
1. Encapsulating Agent
2. Graphite Cathode
3. Impregnated Fiberfrax
4. Graphite Anode



SKETCH OF TEST CELLS A12 - 13

Cell Legend

1. Tungsten Cathode Lead
2. Sealing Agent
3. Graphite Cathode
4. Insulating Paper
5. Impregnated Fiberfrax
6. Nickel Cup and Anode

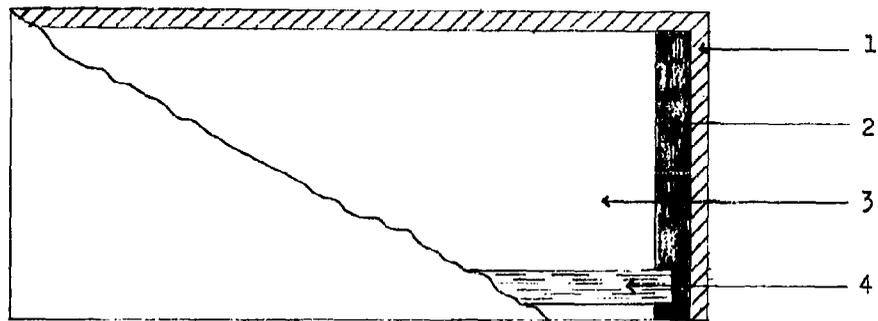


REGENERATIVE THERMOGALVANIC CELL WITH
METAL TO METAL SEAL

Cell Legend

- | | |
|---|---|
| 1. Metal (high nickel content) Cathode Lead | } Comprise
Commercial
Metal-ceramic
Cathode Lead |
| 2. Ceramic (impervious) | |
| 3. Metal (high nickel content) Flange | |
| 4. Nickel Cover | |
| 5. Metal-Metal Seal (heliarc or silver solder) | |
| 6. Ceramic (secondary insulator) | |
| 7. Metal to Metal Seal (heliarc or silver solder) | |
| 8. Graphite Cathode | |
| 9. Impregnated Fiberfrax | |
| 10. Nickel Anode and Container | |

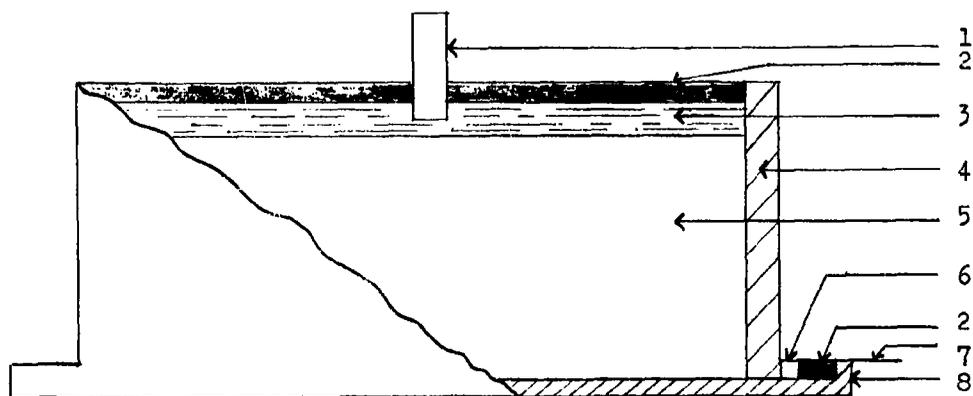
Figure 11



REGENERATIVE THERMOGALVANIC CELL WITH
METAL TO CERAMIC SEAL (Type 1)

Cell Legend

1. Molybdenum Cup (cathode)
2. Sealing Agent
3. Impregnated Fiberfrax
4. Nickel Anode

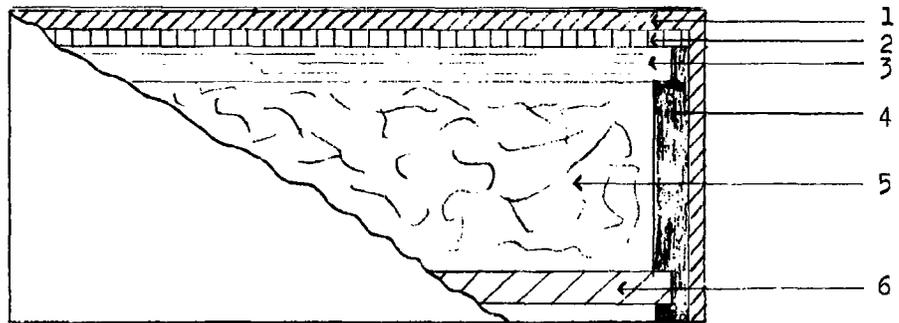


REGENERATIVE THERMOGALVANIC CELL WITH
METAL TO CERAMIC SEAL

(Type 2)

Cell Legend

1. Tungsten Wire (cathode lead)
2. Sealing Agent
3. Graphite Cathode
4. Coors Volcanous Ceramic Ring
5. Impregnated Fiberfrax
6. Silver Paint
7. Nicel Anode Lead
8. Nickel Cup (anode)

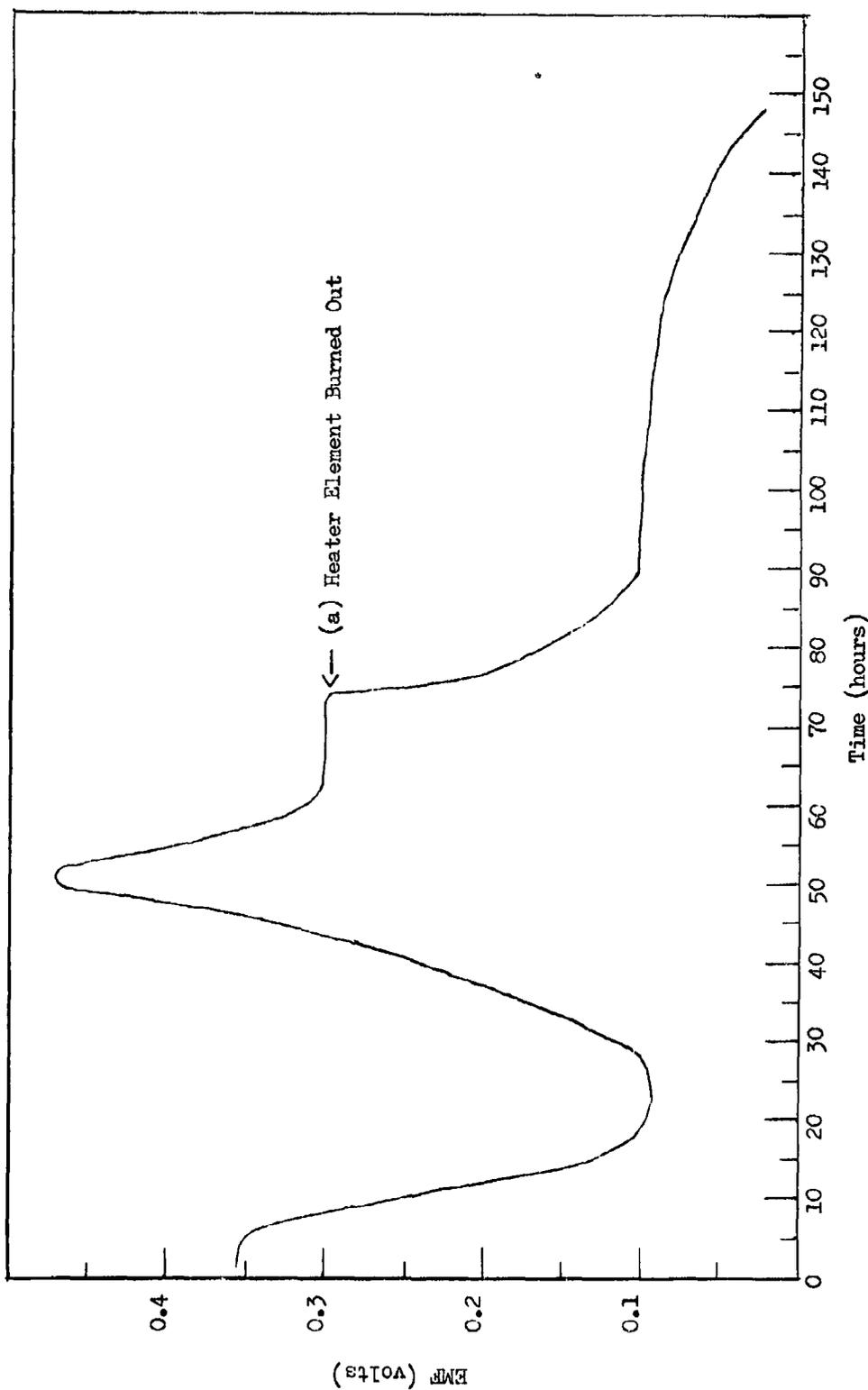


REGENERATIVE THERMOGALVANIC CELL WITH
METAL TO CERAMIC SEAL (Type 3)

Cell Legend

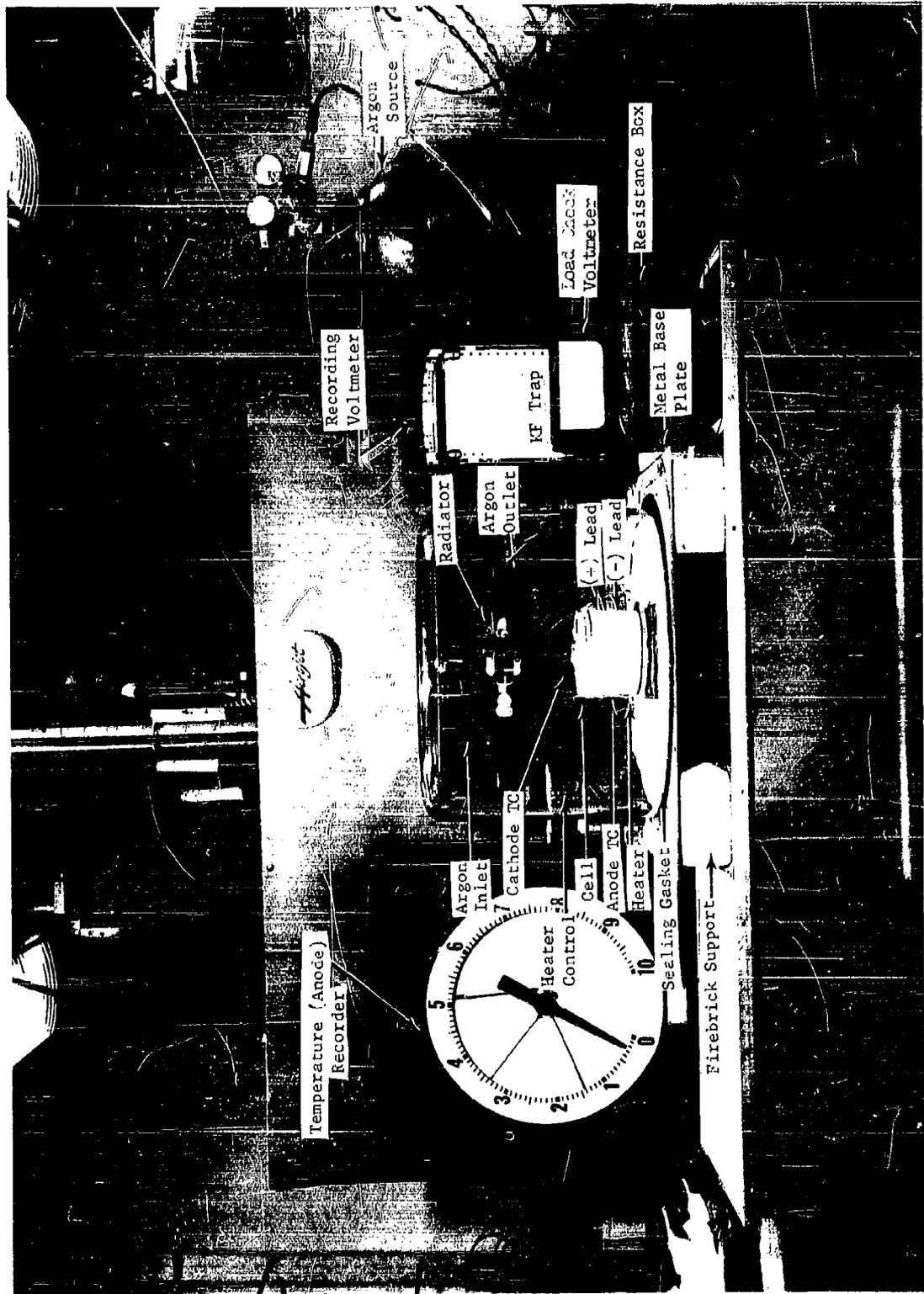
1. Inverted Molybdenum Cup
2. Thermon (a graphite paste)
3. Graphite Cathode
4. Sealing Agent
5. Impregnated with Fiberfrax
6. Nickel Anode

Figure 14



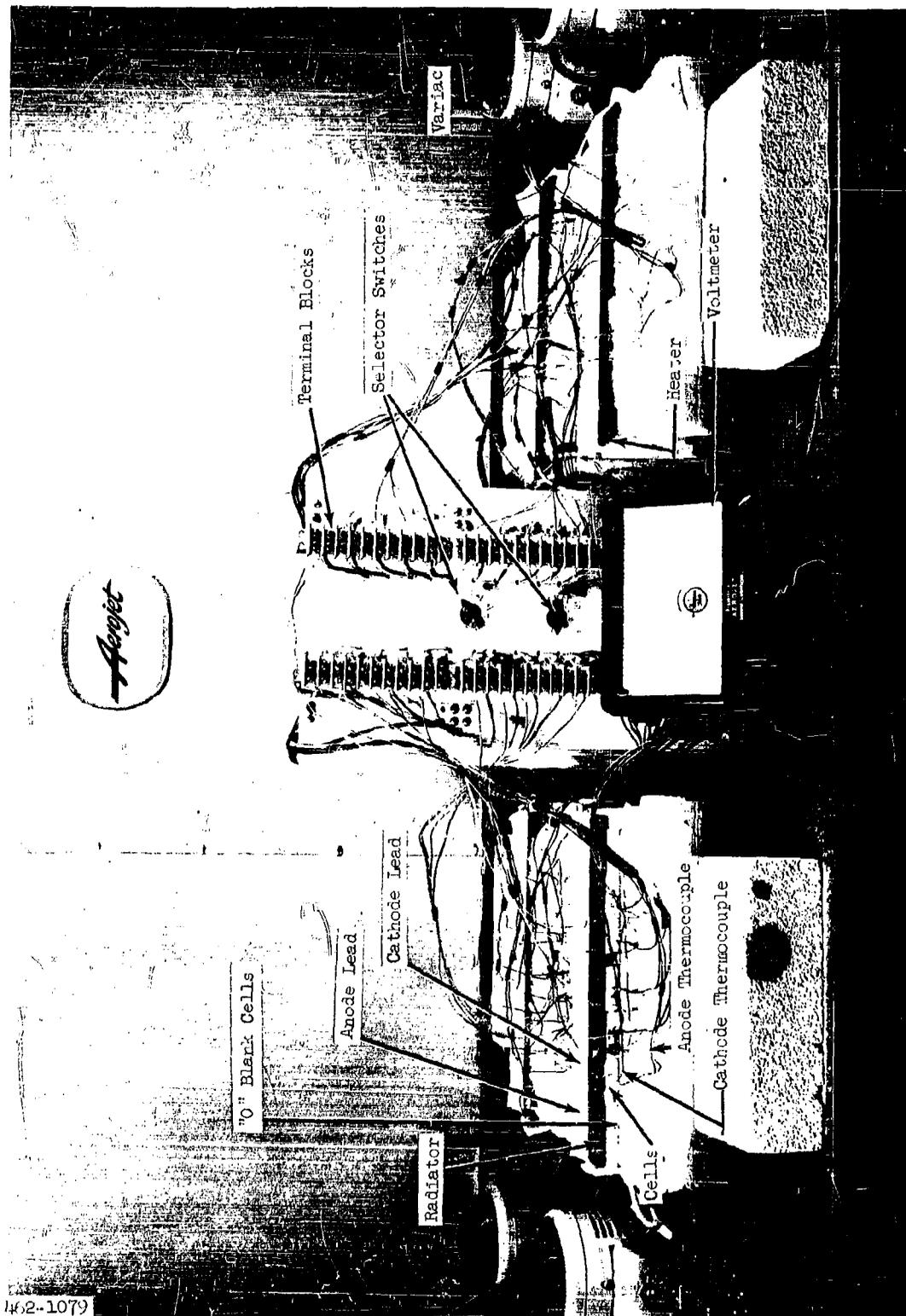
EVALUATION OF CELL NO. 23 (test in air)
(Volts vs Hours of Operation; Load 415 Ohms)

Figure 15



ARGON TEST APPARATUS

Figure 16



Evaluation Apparatus - 20Cell Test
(Test in Air)

Figure 17

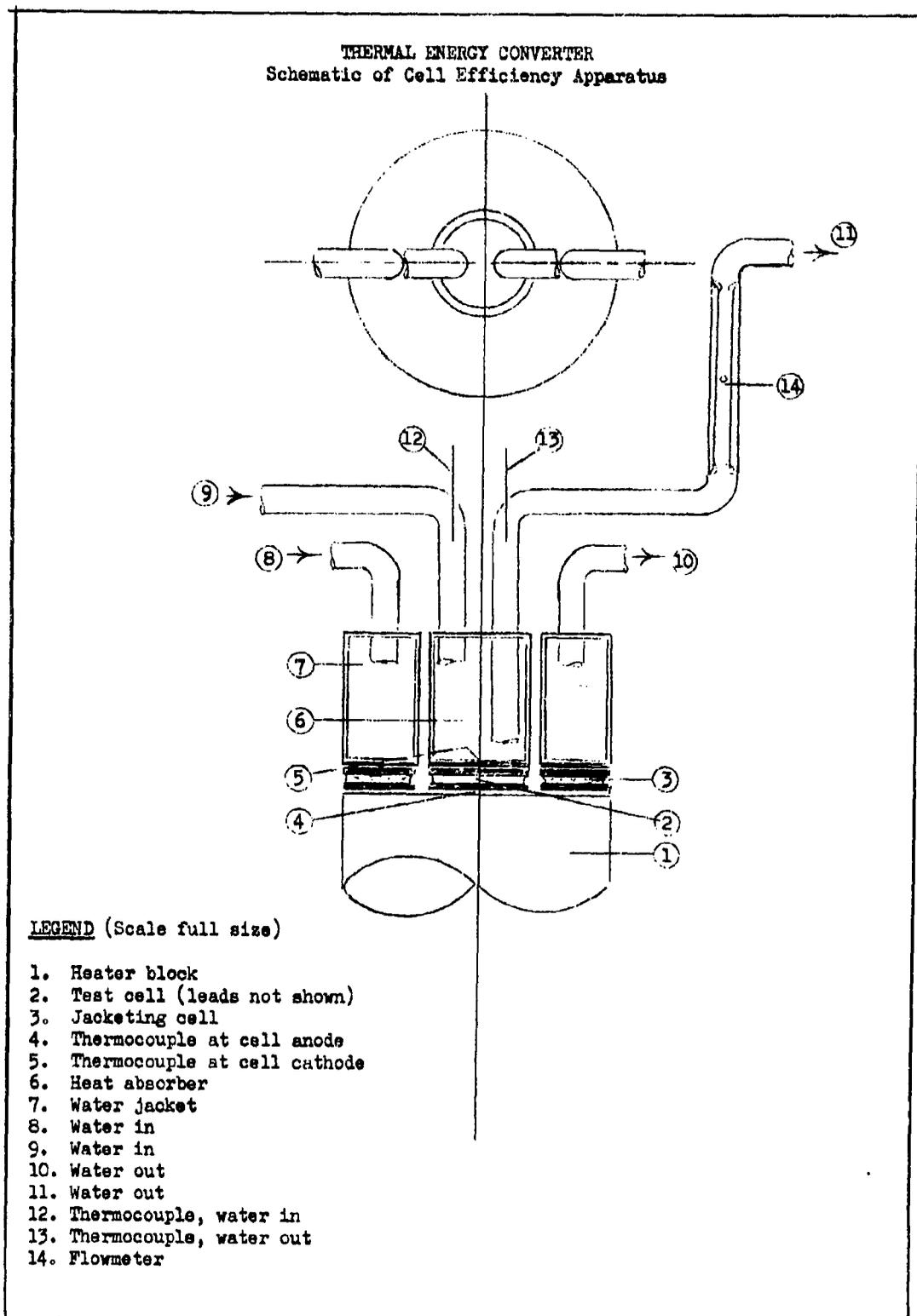
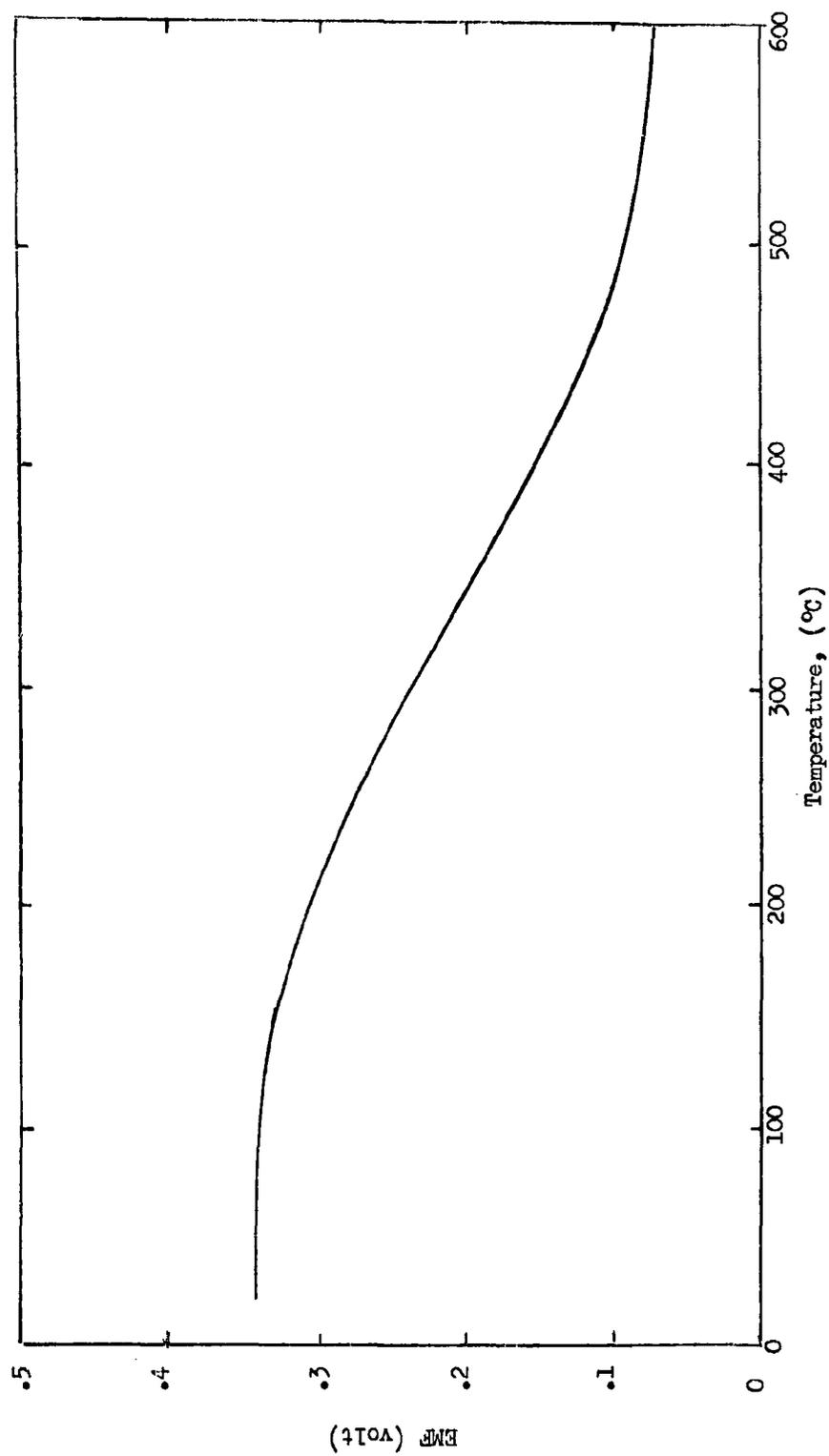
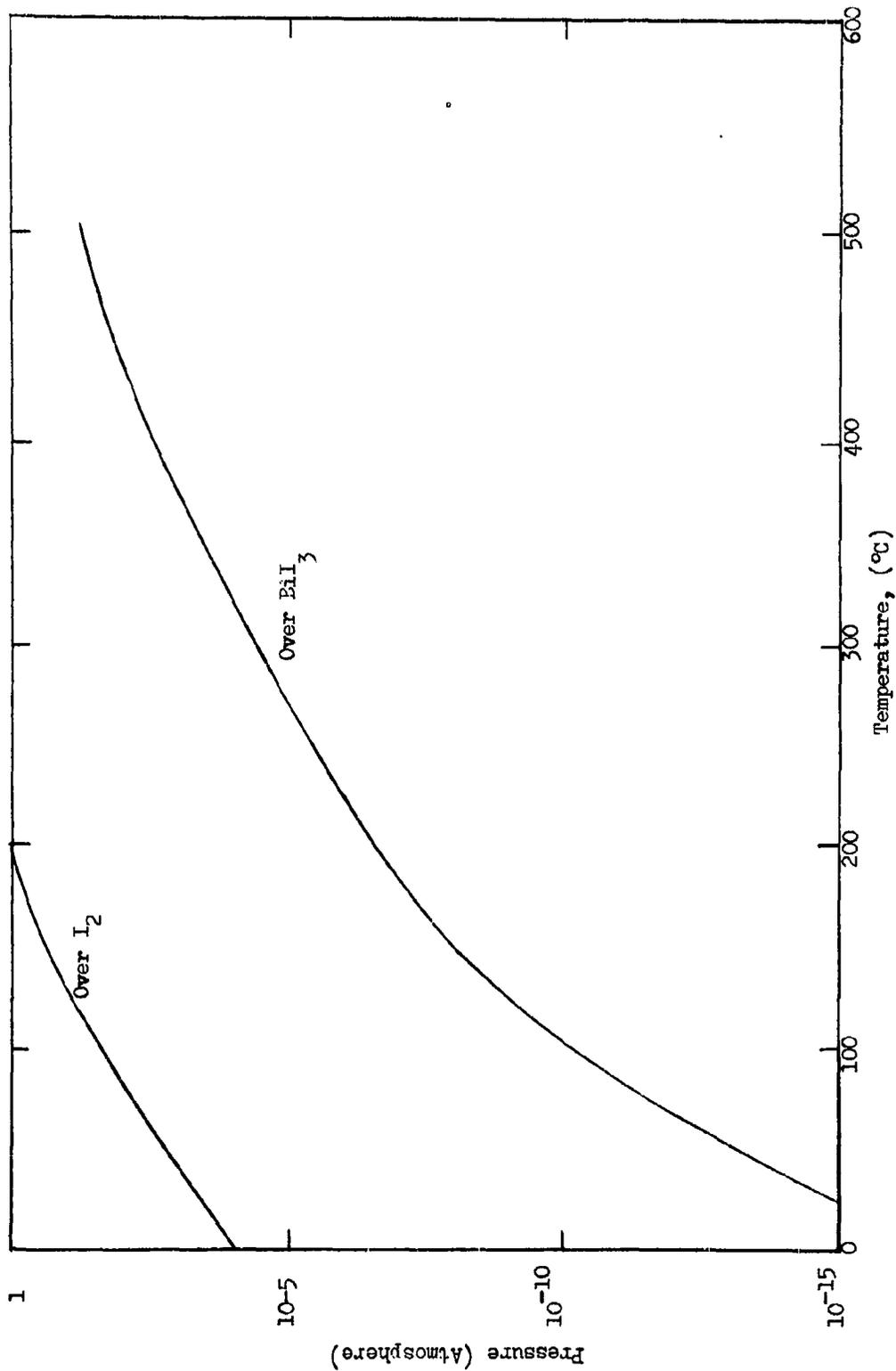


Figure 18



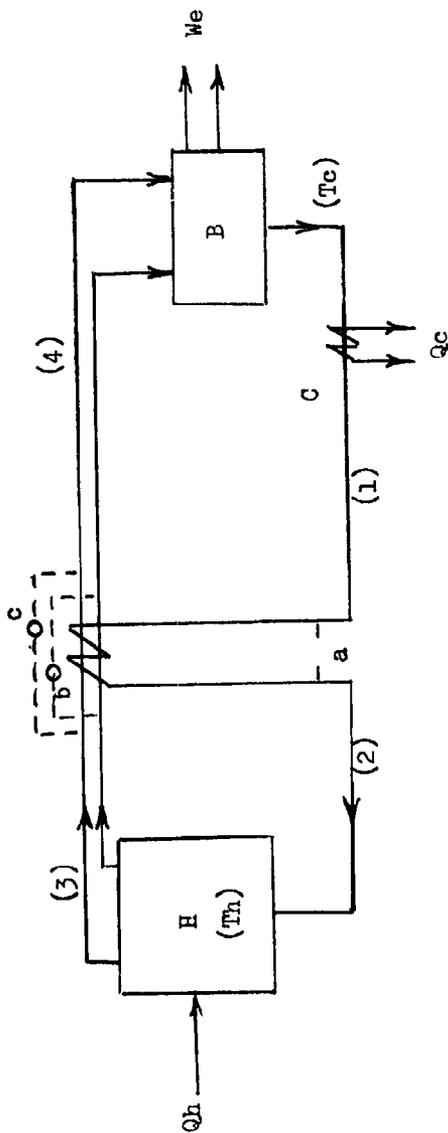
THEORETICAL EMF vs TEMPERATURE OF IDEALIZED THERMAL ENERGY CONVERTER
(Calculated EMF for $\text{Bi} + \frac{3}{2} \text{I}_2 = \text{BiI}_3$, from Data in Quill)

Figure 19



THEORETICAL VAPOR PRESSURE VS TEMPERATURE OF IDEALIZED THERMAL ENERGY CONVERTER
 (I₂ over I₂ and I₂ over BiI₃, calculated from data in Quill)

Figure 20



Cell Legend

- H, Hot Reservoir
- X, Heat Exchanger
- C, Cold Reservoir
- B, Cell

IDEALIZED REGENERATIVE THERMODYNAMIC FUEL CELL

Figure 21

APPENDIX

THERMODYNAMIC CONSIDERATIONS

The thermodynamic properties of bismuth iodide are not well known. However, the data have been reviewed and summarized by Brewer, et al.* From these data it is possible to calculate the potential of the Bi - I₂ - BiI₃ cell as a function of temperature. Figure 19 illustrates the results; the voltage given is the calculated reversible potential for the reactants and products at one atmosphere and unit activity, in their standard states at the temperature of interest. This calculation neglects the effects of sub-iodides of bismuth. It is virtually certain that these exist at high temperatures; the effect of their formation on the details of the thermal dissociation is one of the factors to be determined.*

It has been observed that the total pressure over BiI₃ reaches one atmosphere at 500°C. (See the following tabulation for some physical properties of the materials used.) Figure 20 illustrates the fact that if bismuth iodide decomposed only to Bi + 3/2 I₂, the pressure at this temperature would be only 0.08 atm (the vapor pressure of bismuth is negligible at this temperature). Thus the implication that the triiodide decomposes to lower iodides is reinforced. However, at lower temperatures it appears that the lower iodides disproportionate to the elements and the triiodide. Because of the paucity of experimental data on the halides of bismuth, it is difficult to perform a more detailed analysis of the particular chemical system.

PHYSICAL CONSTANTS OF MATERIALS

<u>Component</u>	<u>Material</u>	<u>Specific Gravity</u>	<u>Melting Point</u>	<u>Boiling Point</u>
Depolarizer	Iodine	4.9	114°C	183°C
Electrolyte	Fused salts	2.9	150°C	730°C
Anode	Bismuth	9.8	271°C	1470°C
Product	Bismuth triiodide	5.7	439°C	500°C (decomp)

* Quill, L. L. Chemistry and Metallurgy of Miscellaneous Materials; Thermodynamics, New York, McGraw-Hill, 1950, p. 251.

The thermodynamics of thermally-regenerative fuel cell systems have been discussed extensively. Friauf* correctly deduces the conditions for achieving Carnot cycle efficiency when both reactants and products are perfect gases. It is important to note that his conclusions are not necessarily as restrictive as they seem, when one or more of the participants in the reactions is a condensed phase. This point is brought out in the EOS work,** in which it is shown that Friauf's necessary condition for Carnot efficiency is correct, but that it reduces in a number of important cases to the special condition $\Delta C_p = 0$. One of these cases has been the basis for the analyses of the BiI_3 system made at Aerojet - i.e., the case that the cell reaction product and one of the reactants obtained from it by thermal regeneration are condensed phases, and that the other reactant obtained is either a gas or a nonsoluble phase, capable of being separated at equilibrium at the high temperature. This latter point seemed so obvious that no great emphasis was given to it in previous discussions of the system. If ΔC_p is not zero, then the ultimate efficiency is less than the Carnot cycle efficiency; in practical cases, however, it is only insignificantly less so; and the practical efficiency reductions from the operation of the cells, imperfect heat exchangers, the pumping energy, and possibly, the need to carry electrolyte through the cycle, would be of greater importance.

One of the great advantages of a primary battery as an energy source is that it is not limited by the Carnot Cycle efficiency. The total heat that would be evolved in the direct combination of anode and cathode reactants R_a and R_c to give cell reaction product P is just $-\Delta H$ for the reaction under the specified conditions. If, on the other hand, they are combined in a cell, the maximum electrical work available is $-\Delta F = nFE$. The difference, $-\Delta H + \Delta F = T\Delta S$, is the excess heat produced by the reaction and is absorbed by a cold reservoir at the cell operating temperature. The efficiency is the ratio of work available to the heat that would be liberated if the reactants formed product without doing any work, or $\Delta F/\Delta H$. (This ratio can be, and in fact is in some cases, greater than unity,

*Friauf, J. B., J. Applied Physics, 32, 616-20 (1961).

**"Investigation of New Solar Regenerative Fuel Cell Systems," Second Semi-Annual Report, Electro-optical Systems, Inc. Contract DA36-039 SC-87425, January, 1962.

notably in the case of the common lead-acid storage battery and the LeClanche cell. In these cases the reversible discharge of the cell requires absorption of heat at the cell temperature. This fixes the sign of the entropy change and hence of the temperature coefficient of free energy change such that its magnitude increases with temperature. Here, heating the reaction products will not bring them to equilibrium with the reactants.)

Consider now that the cell reaction products are such that they can be heated reversibly, without reaction, to a temperature at which they will dissociate reversibly into the original reactants, be separated at the high temperature, and then be cooled reversibly to the original conditions. Then the entire system is in the original state, and a quantity of electrical work has been produced by the absorption of a quantity of heat at high temperature and the wasting of a fraction of it at low temperature. The ultimate efficiency of this process (namely the ratio of the work done to the heat absorbed) is just $\Delta T/T_h$ by the standard Carnot Cycle arguments.

The question now rises whether the efficiency of the ideal regenerative fuel cell described above is also still given by $\Delta F/\Delta H$ at the cell operating conditions. The following discussion will show that this is indeed the case; the ultimate theoretical efficiency is given by

$$\eta = \frac{\Delta F_c}{\Delta H_c} = \frac{\Delta T}{T_h}$$

However, the primary expression of the efficiency is the ratio of free energy change to enthalpy change for the reaction at the cell temperature chosen. The high temperature is thereby fixed as the temperature at which the free energy change for the reverse of the cell reaction is zero, and is hence a dependent variable of the thermodynamic properties of the cell reactants.

1. Consider the idealized system shown in Figure 21. A series of reversible steps will be undertaken as follows:

One mole of reaction product, P, at point (1) of the cycle is at cell and reservoir temperature T_c . A portion of the product, n, passes through the perfect countercurrent heat exchanger X and is heated to T_h , the temperature of the hot reservoir H, at which $\Delta F_h = 0$. The enthalpy change associated with this process may be expressed as

$$\Delta H_x = n \int_{T_c}^{T_h} C_p(P) dT^* \quad (1)$$

The remainder of the product, m , bypasses the exchanger through "a" and remains at T_c . (Alternatively, bypass (a) could be closed and bypasses (b) and (c) opened depending on the relative heat capacities of the product, P , versus that of the reactants R_a and R_e . The argument is similar.)

Streams n and m then mix to give a net temperature T_2 which is different than T_h . The net enthalpy change then from (1) through (X) to (2) may be represented as

$$\Delta H_x = \Delta H_2 = n \int_{T_c}^{T_h} C_p(P) dT + n \int_{T_h}^{T_2} C_p(P) dT + m \int_{T_c}^{T_2} C_p(P) dT \quad (2)$$

but since $n + m = 1$

then

$$\Delta H_2 = \int_{T_c}^{T_2} C_p(P) dT \quad (3)$$

Thus 1 mole of product P enters H at a net temperature different than T_h .

Energy must be applied to product P to raise the temperature from T_2 to T_h . The enthalpy change may be shown by

$$\Delta H_H = \int_{T_2}^{T_h} C_p(P) dT. \quad (4)$$

If this heat is supplied at the hot reservoir temperature T_h , then an irreversible heating occurs, and the Carnot efficiency is not realized. It will be seen that $T_2 = T_\eta$ if ΔC_p for the reactants and product is zero; under these conditions Carnot efficiency is attainable in principle. However, ΔC_p , if not zero, is usually small and causes small reduction in efficiency.

* For simplification in the mathematical treatment, the integral heat capacity expressions are taken to include implicitly the enthalpies involved in all phase changes which may be encountered in the process.

In H, the mole of product P is decomposed reversibly into products R_a and R_e at T_h by the absorption of heat as follows:



The source of heat for equations 4 and 5 is Q_h , hence

$$Q_h = \Delta H_R + \Delta H_H \quad (6)$$

R_a and R_e pass out of H in separate streams to point 3.

The enthalpy change from point 2 to point 3 may now be represented by

$$\Delta H_3 = \Delta H_H + \Delta H_R = Q_h \quad (7)$$

It is assumed, as is necessary, the P and either R_a or R_e are condensed phases at temperatures up to T_h . Decomposition during heating P is prevented by maintaining the pressure at the value corresponding to the decomposition pressure at T_h , and R_a and R_e are separated at T_h by their difference in phase, to prevent recombination during cooling. R_a and R_e pass in separate streams through the perfect heat exchanger (X) and are cooled to T_c . The enthalpy change in the process is

$$\Delta H_{X'} = - \int_{T_c}^{T_h} C_p(R_a) dT - \int_{T_c}^{T_h} C_p(R_e) dT \quad (8)$$

Since we have assumed a perfect countercurrent heat transfer unit, then

$$\Delta H_{X'} = -\Delta H_{X'} = \Delta H_2 \quad (9)$$

and from Equations (3) and (8)

$$\int_{T_c}^{T_2} C_p(P) dT = \int_{T_c}^{T_h} C_p(R_a) dT + \int_{T_c}^{T_h} C_p(R_e) dT \quad (10)$$

The streams enter the cell, C, with a total enthalpy change ΔH_c which is the sum of the enthalpy changes from Position 1 to 2, 2 to 3, and 3 to 4, or from Equations (3), (7) and (8)

$$\Delta H_c = \Delta H_2 + \Delta H_3 + \Delta H_x, \quad (11)$$

but from Equation (9), $-\Delta H_x = \Delta H_2$

Therefore,
$$\Delta H_c = \Delta H_3 = Q_h \text{ (from Equation (7)).} \quad (12)$$

But ΔH_c can be identified with the enthalpy change for the reactants going to products at the cell temperature, as it is a state function and must be the same by any reversible path.

In the cell, R_a and R_c react to produce an electric energy $-\Delta F_c$. At the same time, a quantity of heat Q_c is liberated to the cold reservoir C. Then

$$Q_c = -\Delta H_c + \Delta F_c = -T_c \Delta S \quad (13)$$

The system is now in its original state and the efficiency of the system, if $\Delta C_p = 0$, must be equal to the Carnot Cycle efficiency, i.e.

$$\eta = \frac{W_e}{Q_h} = \frac{T_h - T_c}{T_h} \quad (14)$$

Since W_e , the electrical work produced, is ideally $-\Delta F_c$ and from Equation (12) $\Delta H_c = Q_h$, then

$$\eta = \frac{W_e}{Q_h} = \frac{\Delta F_c}{\Delta H_c} = \frac{T_h - T_c}{T_h} \quad (15)$$

2. Note that if electrolyte must be carried through the cycle with the primary working materials, the only losses entailed will be from second-order effects. The sensible heat carried out of H by the working fluid will be returned to the incoming stream in the heat exchanger X, and the only losses will be from the requirement for additional pumping power and from additional irreversible entropy generation in the practical heat exchanger.

3. If the hot reservoir temperature had been chosen below that at which ΔF for the reverse of the cell reaction was zero, then reversible decomposition of the products into reactants at the constant pressure selected could not occur, and the analysis would not apply. If, on the other hand, T_h had been arbitrarily chosen to be higher than that demanded by the analysis (implying greater efficiency), the additional potential work would not be realized. It is seen that the efficiency is determined by the characteristics of the cell reaction; at the temperatures required by these characteristics the cycle described is a Carnot cycle and the efficiency is also described by $\frac{\Delta F}{T_h}$. However, at other arbitrary temperatures, the full potential of the Carnot cycle is not realized.

4. If the products and reactants are solids at some point of the cycle, mechanical problems rise which in no way affect the validity of the conceptual analysis. Changes in state are included implicitly in the expressions $\int C_p dT$. Note that the analysis has been carried through in terms of a physically realizable system. No reference to this is required, as the following shows:

a. Reactants at constant pressure and temperatures, T_c , are made to produce, by a reversible process, useful work, W_e , which is just $-\Delta F_c$

$$R_a + R_e = P, \quad -\Delta F = W_e$$

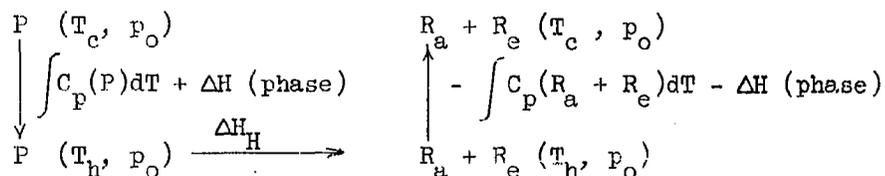
b. The products P are returned to the original state by a reversible process with only the net absorption of heat, Q

$$P = R_a + R_e \quad -\Delta H_c = Q$$

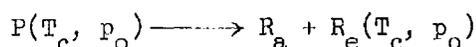
c. The efficiency of the process is

$$\frac{W_e}{Q} = \frac{\Delta F_c}{\Delta H_c}$$

d. A particular reversible process applicable to Paragraph b. is the reversible heating of the product without dissociation, the reversible decomposition of the product, the separation of the reactants at equilibrium, and the reversible cooling of the reactants $R_a + R_e$ to the original temperature



The net heat absorbed is the sum of these three steps; it is also just the enthalpy difference for the reaction:



or ΔH_c . The dependency of the variable, T_h , on the thermodynamic properties of the cell reactants is obvious from this; it must be that at which the products and reactants are at equilibrium at the pressure chosen, that is, at which $\Delta F = 0$.

5. The ideal efficiency derived above will not of course be obtainable in practice. The major factors that will reduce it are discussed below.

a. With a fixed hot-reservoir temperature, a system in which ΔC_p for product and reactants is not zero will have irreversible entropy generated in heating from T_2 to T_h (Equation (4)). This will be a minor contribution to the inefficiency of the system.

b. The electrical work produced by a practical cell will be less than $-\Delta F_c$, but not less than half of $-\Delta F_c$. A cell or battery can be operated at close to maximum theoretical efficiency, with a large weight penalty, or at maximum power output with savings of weight, but with only 50% of maximum efficiency. The actual optimum operating point for the system depends upon the relative importance of battery weight and regenerator weight. In the parallel case of a non-regenerative fuel cell, the optimum operating point depends upon the relative importance of battery weight, reactant weight, and operating time.

c. Another cause of less-than-theoretical efficiency is imperfection in the heat exchanger. Thus, unless the temperature differences along the heat exchanger are infinitesimal, irreversible entropy is generated by the process. It could be an important item because, although countercurrent heat exchangers can be made to approach 100% efficiency, they thereby become quite heavy. For a weight-limited system, a tradeoff will be required for lowest system weight.

d. For a large system, auxiliary power will be required to effect the necessary mass transfer of products, reactants, and electrolyte. This will effectively reduce the overall efficiency. The magnitude of the reduction depends upon the particular system envisioned, but should be small.

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