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Final Report

STUDY OF MULTIPLE RESERVE ELECTROCHEMICAL POWER SOURCES

By

W. N. Carson, Jr.
H. A. Christopher

August 1968

Prepared for

HEADQUARTERS
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C.

CONTRACT NAS 7-674

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RESEARCH AND DEVELOPMENT CENTER
SCHENECTADY, NEW YORK

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NOTICE

Requests for copies of this report should be referred to:

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Attention: AFSS-A

FOREWORD

This final technical report covers work performed between May 22, 1968 and August 30, 1968 under Contract NAS 7-674, "Study of Multiple Reserve Electrochemical Power Sources." It has been prepared by the Research and Development Center, General Electric Company, Schenectady, New York for the National Aeronautics and Space Administration.

Dr. R.C. Osthoff, Manager of the Electrochemistry Branch, in the Physical Chemistry Laboratory of the Research and Development Center, was Program Manager. The program was under the technical direction of Dr. W.N. Carson. Detailed studies on the indicated systems was carried out by the following members of the Research and Development Center:

Metal-Oxygen Cell Systems

Dr. H.A. Christopher
Dr. W.F. Mathewson

Lithium-Cupric Sulfide Cell System

Dr. H.A. Catherino
Dr. R.P. Hamlen

Lithium-Selenium Cell System

Dr. W.N. Carson, Jr

Computer Equations and Programs

Dr. W.N. Carson, Jr
Dr. H.A. Christopher
Mr. E.C. Jerabek
Mr. J.F. Wilfore

The information and help received from the following contributors is gratefully acknowledged:

Dr. G. Gerbier	SAFT — Poitiers Research Laboratory
Dr. M. Gabano	SAFT — Poitiers Research Laboratory
Mr. F. Parker	SAFT — America
Dr. E.J. Cairns	Argonne National Laboratory
Dr. A. Tevebaugh	Argonne National Laboratory
Dr. H. Shimotake	Argonne National Laboratory
Dr. R. Walker	University of Florida
Mr. P. Voyentzie	Battery Business Section General Electric Company

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Section 1

SUMMARY

The feasibility of the multiple reserve operation of batteries used for space power supplies was examined by making detailed studies on three high-energy density galvanic cell systems: lithium-cupric sulfide, lithium-selenium, and metal-oxygen. The analysis of these cell systems showed that multiple activation of a single large battery is not a useful approach, particularly where the activation is by heating. In no case examined was it possible to make significant savings in overall weight, and the extra complexity markedly decreased overall reliability of the power supply. The general design most suitable for accomplishing the goal of a multiple reserve power supply in a single package is the design which calls for separate activation of each section.

All three systems are relatively new but are in an advanced state of development. The lithium-cupric sulfide cell employs a nonaqueous electrolyte; this cell has been under intensive development by SAFT - Leclanché of Poitiers. The lithium-selenium cell is a high-temperature cell, using a molten salt electrolyte; this cell has been developed at Argonne National Laboratory. The metal-oxygen cell study was restricted to zinc and aluminum as anodes. Sufficient data on each of the cell systems were available to allow a relatively complete analysis. However, because of the newness of the systems, a large amount of work needs to be done on each system before it can be used for space missions.

The study of the three systems shows that the lithium-selenium system offers the most promise for a high-energy, multiple reserve power supply. This system is activated by heating to the operating temperature of 375° C. In the design study, a boron-vanadium pentoxide mix delivering 750 calories per gram at 375°C was used as the heat source material. Optimization of the system design with respect to weight was made using a computer programmed to determine the system weight in terms of system and mission parameters. The latter were taken as 1, 10, 50, 100, 200, 500 kilowatt-hours capacity, 5 to 10 activations, and 100, 200, and 500 watt outputs. The optimum (e. g., minimum) weight for each of the 108 missions, defined by the mission parameters, and for each system were computed. The values of energy density varied with the mission. The comparison of the energy values allowed the clear choice of the lithium-selenium system. Typical energy densities for all but the 1000 - watthours capacity were over 190 watthours per pound, ranging to 270 watthours per pound for favorable missions.

The corresponding analysis for the two metal-oxygen systems favors zinc as the anode metal, largely because of the lower amount of heat generated; the energy densities range from 40 to 50 watthours per pound to 160 to 170 watthours per pound over the mission spectrum. Reuse of the water for activation can save up to 10 percent of the weight, but only at the cost of major complexity in deactivation and clean up of the electrolyte.

The analysis for the lithium-cupric sulfide system employing a tetrahydrofuran-lithium perchlorate electrolyte gives energy density values of 2.8 to 150 watthours per pound over the mission spectrum. The low energy density results largely from the low specific discharge rates possible, plus the relatively large self-discharge losses. The data available for analysis of this system were sparse, but sufficient to make an analysis. It is unlikely that additional data will change the relative position of the system with respect to energy density.

The use of power conditioning equipment can reduce the size of the power system and improve reliability by making it possible to use a battery design with a minimum number of cells in series. Such a battery design saves on cell case and terminal weight, on activation equipment, etc. This saving is partially lost because of the electrical losses in the conditioning equipment and the weight of the conditioning equipment. However, for automatic activation, it may be possible to show substantial savings in overall weight resulting from reductions in the cell and activation structural parts. The use of such power conditioning equipment was considered as part of the analysis of the power system.

Section 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. The design analyses made for the three galvanic cell systems show that the concept of multiple activation of a single, large battery is inferior in energy density for most cases and, in all cases, in reliability and complexity to activating only a part of the battery each time. This presupposes that each mission is sufficiently programmed to allow dividing the power supply capacity into the proper sized sections so that waste (unused capacity per activation) is held to a minimum.

2. Any savings in weight of the battery components made possible by multiple activation will probably be lost due to the weight of the activation equipment. In the case of all three systems, automatic deactivation leads to a number of severe problems, such as degradation of the cell during storage.

3. The lithium-selenium cell system shows the largest energy densities for the 108 missions of the three cell systems examined. The relative values, on the average, are: lithium-selenium 100; metal-oxygen 60; lithium-cupric sulfide 50.

4. Although the design analysis for the lithium-selenium cell system required some extrapolation from the current design (particularly regarding cell size), the amount of extrapolation was relatively small, and there is no reason to expect any basic design limitations in developing a power supply for space applications. Use of the cell on a one-shot basis reduces the problems of sealing at elevated temperatures, because the seal has to be in effect for only one thermal cycle. Pyrotechnic heating is experimentally unverified for large cells; again, the basic design is believed sound; the pyrotechnic material has been well characterized. A "cold" storage life of 20 years is well within reach.

5. The lithium-selenium cell is essentially immune to changes in environment and can be operated over the expected ambient in a single design.

6. The lithium-cupric sulfide cell system lost out in energy density because of the high internal impedance of the non-aqueous electrolyte. The cell system is also affected by ambient temperature and may need cooling at the higher power levels when operating.

7. The metal-oxygen cell systems lost out in energy density because of the need to provide transpirational cooling. These systems, since they employ aqueous electrolytes, also offer difficulties in operating at low temperatures.

RECOMMENDATIONS

A two-part program for developing the lithium-selenium cell for multiple reserve battery application is recommended. The first part should be devoted to perfecting the cell and the heat system design and the second part to adaptation with a heat supply for spacecraft use.

The present state of development of the lithium-selenium cell system is not adequate to support a detailed design and fabrication program for a space power supply. A particular deficiency is the absence of experimental data on the fabrication and operation of large size cells (both in area and ampere-hour capacity) suitable for operation over a one month to six weeks period. Additional information on the thermal capacities, entropy change, voltage temperature coefficient, internal resistance, and fabrication techniques is needed.

A need also exists to match the pyrotechnic heating system to the battery and to develop adequate thermal shielding. These must be well in hand before a space system can be designed and optimized. However, during the development, the needs of the final system must be kept in mind if a truly optimum system is to be obtained.

Specific Items for Cell Development Phase

1. Develop large-capacity electrode/electrolyte hardware.
2. Develop adequate seal/gasket for the cells.
3. Develop fabrication techniques leading to reliable, nongassing cells.
4. Obtain $T\Delta S$, internal resistance, open-circuit voltage temperature coefficient, accurate thermal capacity, and long-term operating data on the cells.
5. Develop pyrotechnic mixture and hardware for heating the cells.
6. Obtain data on the heat content and the temperature excursion of pyrotechnic mixture and the cell combination.
7. Develop the heat shield.
8. Obtain data on thermal losses for the shielding calculations.

The data and information obtained in this phase would be used in designing the space power supply. An exhaustive optimization could be made using computer techniques prior to any hardware fabrication and testing.

Specific Items for Space Power Supply Development Phase

1. Optimize the design of the individual cells for weight, energy density, and reliability.
2. Optimize the hardware design for heat material emplacement, and ignition.
3. Optimize the overall system design, determine the part sizes etc.
4. Construct test systems of adequate size to validate the design.
5. Perform tests.

Completion of this phase would result in a multiple reserve power supply design for space applications which could be readily adapted to most missions.

Section 3

INTRODUCTION

This study was made as part of a program to determine the feasibility of multiple reserve battery operation for space power supplies. The study was made on three different basic cell systems: lithium-cupric sulfide cells, lithium-selenium cells, and metal-oxygen cells. The systems are relatively new, but are in an advanced state of laboratory development. The lithium-cupric sulfide system uses an organic solvent with lithium-perchlorate electrolyte. This cell system is in the semicommercial stage of development. The lithium-selenium cell uses a molten salt electrolyte and operates at 375°C. This cell system is the least developed in that only laboratory models have been built and tested; whereas, manufacturing prototypes and field test units have been constructed and evaluated for the other cell systems. The metal-oxygen cell study was restricted to the use of aluminum and zinc as anodes, with a saline or alkaline electrolyte.

With respect to space applications, none of the present cell systems is developed to the stage where space hardware could be designed or built without a substantial program of additional development. A number of problems which can limit the utility of each system for space applications have been identified; however, no basic design limitation is known that would absolutely preclude the use of any of the systems. The stage of development of each of the systems is such that it is unlikely that such a basic limitation will be uncovered in future work.

MISSION ASSIGNMENT

In making a comparison of the power supplies, it is necessary that the mission or set of missions using the power supply be known. In this study, a set of missions was selected to cover the spectrum of possible missions. In addition, a set of other mission parameters was arbitrarily selected in order to establish the mission requirements for studies on the power supplies. The mission parameters and the assigned values used in the study are shown in Table 1. The six capacity levels, the six activation levels, and the three output levels define 108 separate missions. For each of these missions, the other parameters apply.

The environmental temperature range was set at -20°C to +45°C, because this appears to be the range which can be provided for operation in unmanned spaceships. It is also a temperature range more or less suitable for astronauts to work in using the power supply. Sterilization is specified, but may not be necessary. The storage temperature is taken from military requirements, -65°F to 160°F.

Table 1

MISSION PARAMETERS FOR POWER SUPPLY DESIGN

Temperature	
Inactive storage	-55°C to 85°C
Inactive sterilization	110°C to 145°C
Active operation (environmental)	-20°C to 40°C
Gravity Forces	
Zero "g" or reduced gravity	
Mode of Activation	
Manual	
Semiautomatic	
Automatic	
Number of Activations	5 to 10
Availability of Power to Initiate Activation Process	Yes
Use of Power Conditioning Equipment	Yes
D-c to a-c transformer	
Inverters	
Regulation	
Power Supply Requirements	
Capacity	1, 000, 10, 000 50, 000, 100, 000 200, 000 and 500, 000 watthours
Discharge rate	100, 200 and 500 watts
Total mission time	5 to 10 years -- 20 years desirable

Because of the wide varietv of possible missions, both automatic and manual methods of activation were studied. . It was assumed that sufficient auxiliary power, e. g., solar panel or space suit power, will be available for energizing the activation system. As part of the activation study, the deactivation process was also considered.

The number of activations affects the size of the system, since some weight penalty must be paid for each activation, even though in some systems this may be nearly zero. At present, it is felt that the number of activations should range from a minimum of five to a maximum of ten.. The effect of the number of activations on the weight of the power supply was studied in the system analyses.

The total mission time is of interest because of the losses that may occur during inactive storage. It may be desirable to provide extra features in the design to decrease these losses; the utility of this approach will depend on the storage time and the loss rates. The lithium-selenium cell system would be expected to give the best storage characteristics on two counts: 1) the storage will be made in what amounts to a deep-freeze condition in which the chemical reactivity is very low, thus preventing self discharge, parasitic reactions, and deterioration of the structural parts; 2) the active state calls for both the electrodes and the electrolyte to be in the molten state; this will minimize the effect of any physical changes during storage. The storage of the other two systems will depend upon careful sealing of the empty cell to prevent deterioration of the electrodes, or loss of electrolyte or active material from the reservoirs.

OPTIMIZATION

In the design of power supplies, the designer always has one variable that must be arbitrarily chosen to complete the design. Since the value of this variable can be arbitrarily chosen, it can be selected to "optimize" the system's design with respect to one design feature. Thus, the system weight, volume, or cost can be minimized. In this study, optimization of the power supply was the one with minimum weight, or, in other terms, the one with the highest energy density (watthours per pound). The variable adjusted was the operating cell-voltage.

In making the optimization, the procedure is to design the basic cell hardware -- cell electrodes, electrolyte, separator, casing, and auxiliaries. This basic hardware must in itself be "optimized", i. e., low weight construction consistent with reliability and manufacturability must be built into the design at this point. From this basic hardware design, the parameters used in system optimization are calculated and inserted into the parametric equations for system weight. In these equations, it is convenient to use the operating cell voltage as the independent or slack variable. For optimization (minimum weight), the equation is differentiated and the differential is set equal to zero. The derived equation is then solved analytically for the operating cell voltage or by some iterative method, if the equation is complicated, as it usually is.

For computer solution, it is generally simpler not to take the derivative, but to solve for the proper value of the operating cell voltage by computing the weight using an arbitrary starting value of the operating cell voltage, and then varying this value in small increments across the region for the minimum system weight. The minimum system weight is found by inspection, or by instructing the computer to determine the difference between successive values and find the one that shows a sign change.

The equations relating the power supply weight to various mission and cell parameters are derived using the concept that a power supply (from the analysis standpoint) can be broken down into three basic sections: energy storage, converter, and accessory. Mathematically, all weights that are a linear function of the total energy output can be incorporated into the energy storage term, all weights that are a linear function of the power output can be incorporated into the converter term, and all fixed or slowly variant weights can be incorporated into the accessory term. Some weights (such as the container weight for externally stored active materials, weight of the thermal shields, the cell casing weight, etc) are functions of the volume of that portion of the power supply with which they are associated. These weights enter the equations as the 2/3 power of the volumes, the factor for converting volume to surface.

Table 2 gives the basic equations used in the optimization with respect to weight. The mission parameters and cell parameters are defined in terms of the operating cell voltage and the related cell design features. A numerical solution is possible only if these are assigned. In this study, the minimum weight was found for each mission and used as the figure of merit for system evaluation in the form of watthours per pound. The value of the operating current density, J, for a given operating cell voltage, V, was obtained from experimental data in the form of an equation in V. In making up the computer programs, variations in the equations and the form of the parameters were necessary in order to accommodate the fundamental differences in the systems with efficient programming.

In Table 2, the cell design parameters appear as W's. In assigning the values for these parameters, the kinds of items to be included must be kept in mind. Thus W_1 includes not only the weight of the active cell materials but also the weight of other materials consumed in proportion to this weight, such as electrolyte components, heating material, cooling material, electrode fabrication materials, etc. Parameter W_2 includes excess electrolyte not consumed in operation, separator, electronic collectors, seals, terminals, and activation materials not included in W_1. Similar arguments can be expressed for the other parameters.

Table 2

PARAMETRIC POWER SUPPLY WEIGHT EQUATIONS

Total weight = energy storage weight plus converter weight plus accessory weight

$$S = SA + SB + SC$$

$$SA = \frac{Q}{V}\left(W_1 + \left(\frac{Q}{V}\right)^{-1/3} W_2\right)$$

$$SB = \frac{MP}{JV}\left(W_3 + \left(\frac{P}{JV}\right)^{-1/3} W_4 + \frac{V}{E} \cdot W_5\right)$$

$$SC = \frac{P}{V} W_6 + W_7$$

Where:

E = battery voltage, 28 volts

J = operating current density at V, amperes per square foot

M = number of activations per mission, 5 to 10

P = power output, 100, 200, 500 watts

Q = total energy output, 1, 10, 50, 100, 200, 500 kilowatthours

V = operating cell voltage, volts

W_1 = specific weight of material proportional to energy storage, pounds per ampere-hour

W_2 = weight of container for one ampere-hour sized cell (cell casing plus storage container), pounds per ampere-hour$^{2/3}$

W_3 = specific weight of cell converter material, pounds per square foot

W_4 = weight of converter housing for one cell with watt output, pounds per square foot$^{2/3}$

W_5 = weight of cell end plates, pounds per square foot

W_6 = specific weight of power conditioning equipment, pounds per ampere

W_7 = fixed accessory weight (switches, busbars, etc.), pounds

A minimum in the power supply weight occurs because the weight of the energy storage section varies in the opposite direction from the weight of the converter section as the cell operating voltage changes, while the accessory section weight is essentially constant. Thus, the energy storage weight is minimum for a cell operating voltage equal to the cell open-circuit voltage and increases as the cell operating voltage decreases. For the same cell, the converter system weight is a maximum for a cell operating voltage equal to the cell open-circuit voltage and decreases as the cell operating voltage decreases to a minimum at approximately one-half the open-circuit voltage. (In an ideal cell, the minimum converter weight occurs exactly at the half point.)

In setting up the equations for calculating the power system weight, it was found that a large number of parameters relating to the mission must be assigned. Shifts in the values of these parameters cause shifts in the value of the cell operating voltage for the optimum weight; hence, in general, a power system can be optimized only for one set of mission parameters. However, with a set of missions whose parameters cover a wide range, the analysis of the optimum weights of the corresponding power supplies should indicate both the best power system to use and the magnitude of the penalty paid in certain missions compared to a "standard" mission.

The tapes and programs for the computer runs are stored in the technical director's records for this project and can be made available for future use. However, the programs are all shown in Tables 28 through 31 and can be used as the basis for any future work.

Section 4

STUDIES

LITHIUM-CUPRIC SULFIDE CELL SYSTEM

Basic System Characteristics

Table 3 gives a summary of the cell system. This particular system is the best nonaqueous system in terms of energy and power density that has been reported to date. The work on this system has been performed by members of the SAFT (Société des Accumulateurs Fixés et de Traction, S. A.) laboratory at Poitiers, France (Refs. 1, 2, 3, 4). References 3 and 4 were not physically available for the study. The data used in the study were for the isopropylamine electrolyte, although this is no longer used. The difference in behavior of the cells with new electrolyte will not affect the conclusions, but will raise the performance figures somewhat.

Table 3

LITHIUM-CUPRIC SULFIDE CELL DATA

Anode	Lithium
Cathode	Cupric sulfide
Electrolyte	Lithium perchlorate in isopropylamine (1
Discharge	Two step
Open circuit voltage, theory	2.4 volts
Open circuit voltage, actual	2.2 volts
Theoretical energy density (2	1270 watthours per pound
State of development	Prototype (3

Notes

1) Used in first cells. Now using a mixture of tetrahydrofuran and dimethoxyethane which gives less self-discharge than isopropylamine.

2) For reactants only at theoretical open circuit.

3) Twenty ampere-hour cells are now in limited production. At rated current of about C/100 these give over 100 watthours per pound.

System Analysis

The lithium-cupric sulfide system can be readily adapted for use as a reserve cell; no change in electrode or cell construction is needed. At the time of activation, the electrolyte need merely to be forced into the cell in the classic reserve type of operation. The activated life is shortened by self-discharge involving the cupric ion (Cu^{++}) which is somewhat soluble in the electrolyte and discharges at the lithium anode. Table 4 gives the available data. The self-discharge data are for prototype cells. It is expected that somewhat lower values will be obtained in production types. The capacity falls off rapidly at discharge rates higher than the 300-hour rate shown. The use of a reserve-type construction is the only way this cell system can be stored for prolonged periods of time.

Table 4

STAND LOSSES FOR LITHIUM-CUPRIC SULFIDE CELL(1)

Time on Stand (Months)	Ampere-hour Capacity (2) (IPA)	(THF)	Watthours (3) (IPA)	(THF)	Watthours per Pound (IPA)	(THF)	Percent Capacity (IPA)	(THF)
0	25	25	42	42	114	114	100	100
3 (2160 hrs)	23	25	39	41	107	114	94	96
6 (4320 hrs)	21.5	23.5	34	38	95	108	84	90

1) LI-20 cells, discharge and storage at 20°C.

2) IPA -- isopropylamine electrolyte (data used in study).
THF -- tetrahydrofuran - dimethoxyethane electrolyte (Ref. 2).

3) At 300-hour rate, 22-ohm resistance.

No answer, as of the date of this report, has been received from SAFT on the set of questions on construction, areas, etc. submitted to them at the start of the program. However, a number of personal communications (Ref. 1) and a report (Ref. 2) have been available from which sufficient information could be gleaned to allow an analysis. The other reports (Refs. 3 and 4) have been issued since the start of the study, but have not been received. It is unlikely that further information will change the conclusions drawn from the analysis made in this program.

This system uses a lithium anode, a cupric sulfide cathode, and a tetrahydrofuran-lithium perchlorate electrolyte. The cell discharges in two steps:

$$2\,Li + 2CuS_2 \rightarrow Li_2S + Cu_2S \qquad E = 1.7 \text{ to } 1.9 \text{ volts}$$

$$2\,Li + Cu_2S \rightarrow Li_2S + 2Cu \qquad E = 1.4 \text{ to } 1.7 \text{ volts}$$

The lithium electrode apparently uses a silver mesh support and current collector. The cupric sulfide electrode is unique in that the sulfide is a reasonably good electronic conductor and no additive for conduction is needed. The discharge to free copper also helps keep the internal resistance low.

Table 5

LITHIUM-CUPRIC SULFIDE CELL WEIGHT DISTRIBUTION(1

	Weight (Grams)	Percent
Copper Sulfide (Cathode)	154	36
Lithium (Anode)	47	9
Electrolyte (Isopropylamine + $LiClO_4$)	148	23
Cathode Core, Internal Hardware	36	7
Case and Terminals	125	25
	510	100

1) For LI-70 type cell.

Table 5 shows the reported weight distribution in the two cell types (LI-20 and LI-70) now in limited production. The characteristics of these cells are shown in Table 6.

Table 6

CELL CHARACTERISTICS

Cell	Capacity (Ampere-hours)	Volume (Cubic Centimeters)	Weight (Grams)
LI-20	20	140	175
LI-70	70	400	510

The data in Table 5 indicate that an improvement in cell performance (watthours per pound) may be obtained if a substantial recovery of the electrolyte or its overall reduction in relative amount per cell can be achieved. The latter is the most promising approach.

Table 7 shows the discharge behavior of a LI-20 cell at 20°C. The effect of the relatively high internal resistance (due largely to cell electrolyte) is evident. Only low current-density drain rates are practical with such a cell, i.e., the cell must have a very large electrode area for high discharge rates, say above C/50.

Table 7

LI-20 CELL DISCHARGE

Resistance (Ohms)	Hours(1)	Watts(2)	Ampere-hours	Watthours	Watthours per Pound
22	315	0.14	25	44	120
3	75	0.44	23	36	100
0.5	10	1.60	18	16.5	45

1) To 1.0 volt cutoff

2) Initial rate

System Calculations

In making the initial calculations, the system was assumed to be remotely activated, with no recovery of electrolyte. Separate sections of the battery were used per activation. The normal discharge curve (volts versus current density) was not available; instead, the size equations were based on a curve giving watthours per pound for various discharge curves. This curve, shown in Figure 1, was derived from three discharge-time curves as given by SAFT data from the LI-20 cell. Linear extrapolation for discharges longer than 150 hours was made; a nonlinear extrapolation below 30 hours was made so the curve fell smoothly to zero output.

The following values were calculated directly from the data given in Reference 1.

1. The weight per ampere-hour of the electrode ingredients, the internal connections, and the cathode core was 0.0603 pound per ampere-hour.
2. The weight per ampere-hour of the electrolyte vessel was 0.00178 pound per ampere-hour. That is, it was estimated that the weight of an appropriate container capable of holding enough electrolyte for a single SAFT LI-70 cell was 70 grams.
3. The weight per square foot of electrode area for the electrolyte was 0.151 pound per square foot.
4. The weight per square foot of electrode area for the case and the terminals was 0.16 pound per square foot.
5. The open circuit voltage was given as 2.2 volts.

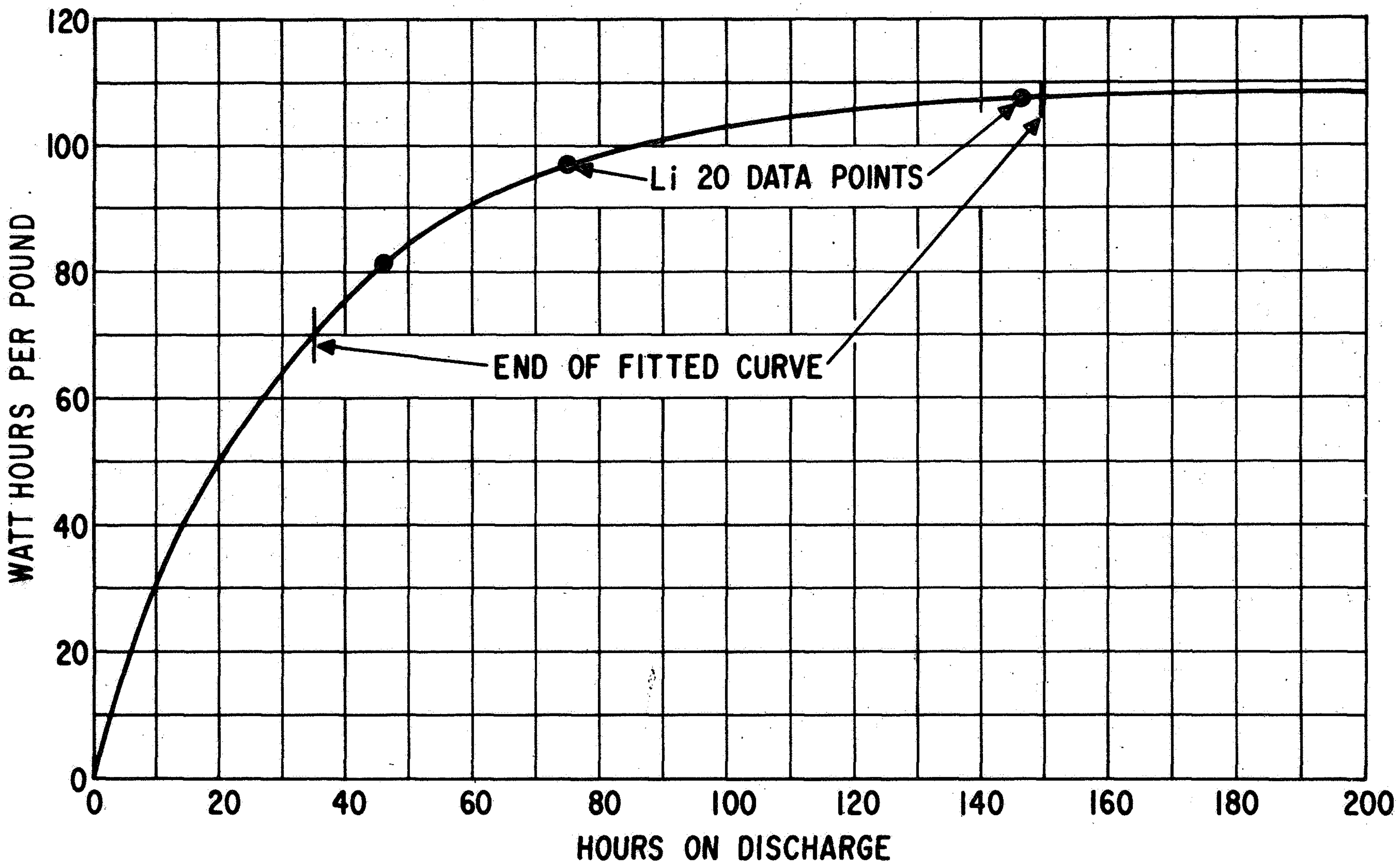

Figure 1. Lithium-cupric Fluoride Cell Discharge Energy Density

The following estimates were made in the absence of specific data:

1. The average resistance of the cell was taken at three ohms. In practice, the cell showed an internal resistance which varied with the rate of discharge and the percentage of the capacity that had already been discharged. The two-step reduction gave the effect of an increase in internal resistance in the latter part of the discharge, since a loss in open-circuit voltage was equivalent to an increase in the IR loss. The internal resistance determinable from the data ranged from one ohm at zero discharge, zero drain rate to seven ohms for fastest discharge.
2. The coulombic efficiencies of the active materials varied as a function of discharge time. These are plotted in Figure 2. The value of the efficiency at the lower discharge times was set arbitrarily at 50 percent, in the absence of specific data. Greater efficiencies are unlikely, lower efficiencies would further reduce the calculated energy densities.

Table 8 gives the program in BASIC. A different program was used in the early studies, but was superseded by the one shown. Table 9 gives an example of a typical run, with the inputs shown. In the program, the ? mark was used by the computer to ask for the value of the input, which was entered into the program manually. In this program, utilization of the anode material was entered as part of the input; the computer gave the value for the result. A second trial was used if necessary to correct the discrepancy. The curve of Figure 2 was used by the operator to obtain the trial values of efficiency. The computer calculated the total system weight for values of V in increments of 0.01 volt and printed out the values when the sign of the difference changed.

Using the program and parameter values, the watthours per pound were computed and tabulated. Table 10 shows the number of watthours per pound obtainable from batteries whose capacities range from 1000 to 500,000 watthours at three different output power levels. The numbers presented are for 5 and 10 activations. In the calculations, it was implicitly assumed that only a single activation can be obtained per battery. Therefore, n activations of the package would require n batteries.

Reactivation of the cell via the removal and subsequent addition of electrolyte does not appear suitable because of the high porosity of the copper sulfide cathodes and the mechanical disintegration of the electrodes, as a result of the joint action of the partial discharges and movements of the liquid.

Table 11 was assembled for argument's sake. It assumes that: 1) the electrolyte can be removed from the cell quantitatively and reused in a subsequent reactivation; and 2) the weight of the auxiliary apparatus required

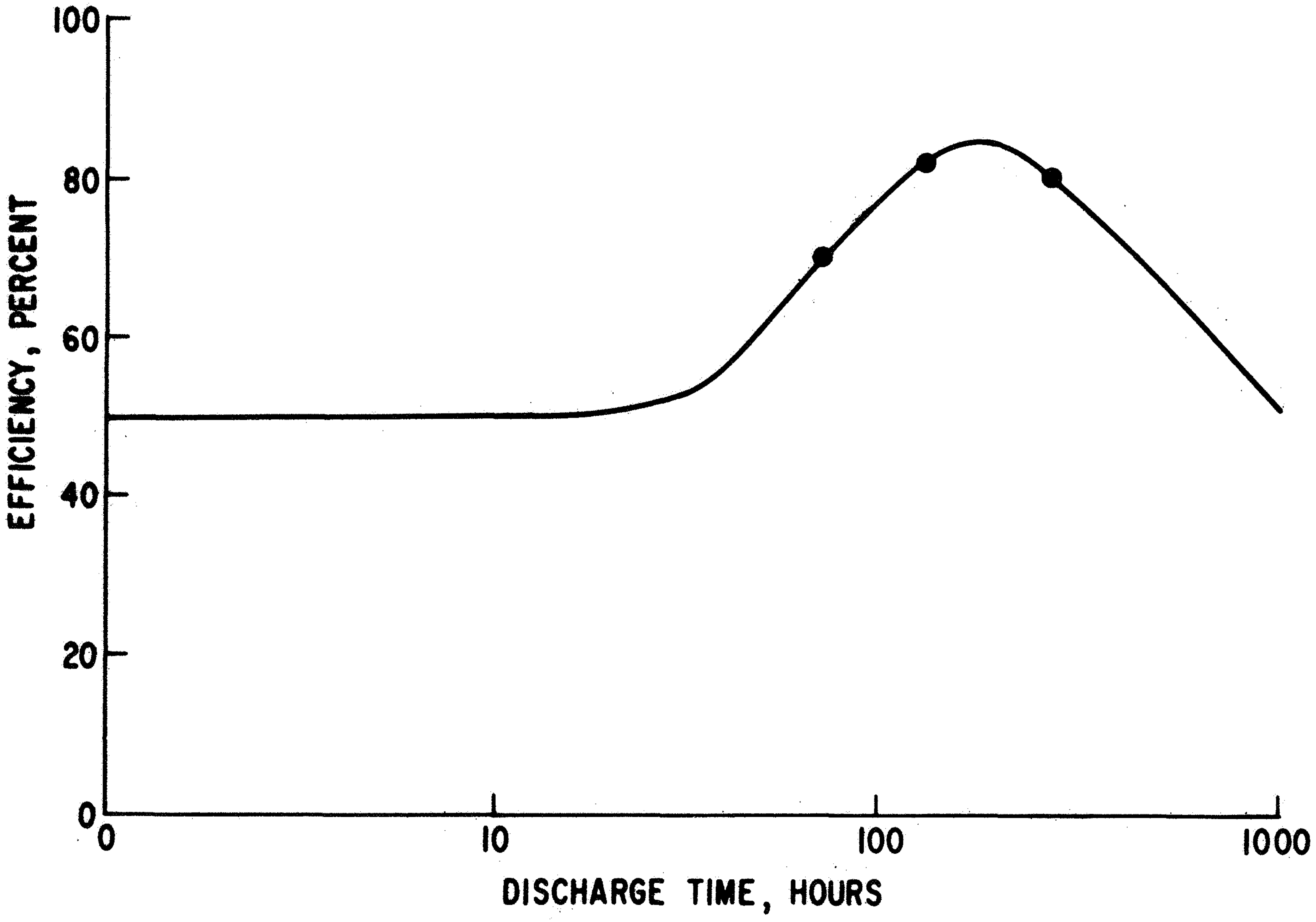

Figure 2. Lithium-cupric Sulfide Cell Utilization

Table 8

LITHIUM-CUPRIC SULFIDE CELL OPTIMIZATION

```
MRPS1     10:10   JULY 12,1968

50 PRINT "               AUXILLIARIES              "
55 PRINT
60 PRINT "VARIABLE AUX. WT, #/AMP------------------";
65 INPUT W0
67 IF W0<0 THEN999
70 PRINT "FIXED AUX WT.  LBS-----------------------";
75 INPUT W
80 PRINT
85 PRINT "               ACTIVATION                "
90 PRINT
95 PRINT "ACTIVATOR CONSUPTION, #/FT.SQ.-----------";
100 INPUT W8
103 IF W8<0 THEN 50
105 PRINT "ACTIVATION STRUCTURE, #/CELL--------------";
110 INPUT W9
115 PRINT
120 PRINT "              CONVERTER                 "
125 PRINT
130 PRINT "ELECTRODES  FRAMES, #/FT.SQ----------";
135 INPUT W6
137 IF W6=0 THEN 85
140 PRINT "CONVERTER HARDWARE, #/FT.SQ/STACK-------";
145 INPUT W7
150 PRINT "CONVERTER LIFE, ACTIVATIONS(PLATES/H'DWR) ";
155 INPUT L6,L7
160 PRINT
165 PRINT "               CELL           "
170 PRINT
175 PRINT "O.C.VOLTS, VOLTS/CELL-------------------";
180 INPUT V(0)
185 IF V(0)=0 THEN 120
190 PRINT "CELL POLARIZATION DATA   "
195 PRINT "DATA PT    I,ASF  V,VOLTS"
200 PRINT "-------    -----  -------"
205 FOR F=1 TO 2
210 PRINTF;
215 INPUT J(F),V(F)
220 NEXT F
225 PRINT "THEO ANODE CONSUMPTION, #/AHR-----------";
230 INPUT W2
235 PRINT "THEO CATHODE CONSUPT'N, #/AHR-----------";
240 INPUT W1
245 PRINT "THEO ELECTROLYTE CONSUM., #/AHR-------";
250 INPUT W3
255 PRINT "EXCESS ELECTROLYTE,NO.  STOICS----------";
260 INPUT N1
265 PRINT "EXCESS ELECTROLYTE RECOVERED/ACTIVATION,0/0--";
270 INPUT R
275 PRINT "WEIGHT OF REACTANT STOREAGE.#/AHR AT 1AHR-";
280 INPUT W5
285  PRINT "ESTIMATED UTILIZATION,P.C. THEO/AHR"
287 LET K=0
290 PRINT "CATHODE/ANODE/ELECTROLYTE---------------";
295 INPUT M1,M2,M3
297 IF K>0 THEN 355
300 LET C=(J(2)/(V(0)-V(2))-J(1)/(V(0)-V(1)))/(V(1)-V(2))
305 LET B=J(1)/(V(1)-V(0))-C*(V(1)+V(0))
310 LET A=-B*V(0)-C*V(0)↑2
315 PRINT
316 PRINT
320 PRINT "               MISSION                  "
325 PRINT
330 PRINT "POWER, WATTS--------------------------";
335 INPUT P
340 IF P=0 THEN 165
343 IF P<0 THEN 999
345 PRINT "CAPACITY, WATT.HOURS-------------------";
350 INPUT Q
355 PRINT
360 PRINT "RATE,HRS", "V/CELL", "I,ASF", "WT.LBS", "WH/LB"
365 PRINT "--------", "------", "-----", "------", "-----"
370 FOR N=5 TO 10
375 LET T=Q/(N*P)
380 LET K6=100*Q*(W1/M1+W2/M2+W3/M3*(1+N1*(1-R/100*(1-1/N))))
385 LET K2=P*W6*INT((N-0.1)/L6+1)
390 LET K3=P/28*W7*INT((N-0.1)/L7+1)
392 LET K4=N*P*W8
395 LET K5=P*W0
400 LET V=V(0)-0.01
405 LET J=A+B*V+C*V↑2
410 LET J1=B+2*C*V
412 LET K7=Q*W5*(V/Q)↑.333
413 LET K1=K6+K7
415 LET D1=(K2*(1+W9)+K4)*(V*J1+J)/((V*J)↑2)
420 LET D2=K3*(1+W9)*J1/(J↑2)
425 LET D3=(K1*(1+W9)+K5)/(V↑2)
430 LET S1=(-1)*(D1+D2+D3)
435 IF S1>0 THEN 445
440 GO TO 450
445 LET V=V-0.01
447 GO TO 405
450 LET S=(K2*(1+W9)+K4)/(V*J)+K3*(1+W9)/J+(K1*(1+W9)+K5)/V+W
455 LET E=Q/S
460 PRINT T,V,J,S,E
465 NEXT N
495 PRINT "CORRECTED UTILIZATION, THEO/AHOUR "
500 GO TO 290
999 END
```

Table 9

SAMPLE COMPUTER RUN LITHIUM - CUPRIC SULFIDE CELL SYSTEM

```
          AUXILLIARIES (SIC)

VARIABLE AUX. WT, #/AMP------------------?0
FIXED AUX WT.  LBS----------------------?   5

          ACTIVATION

ACTIVATOR CONSUPTION, #/FT.SQ. -----------?0
ACTIVATION STRUCTURE, #/CELL--------------?0

          CONVERTER

ELECTRODES  FRAMES, #/FT.SQ----------?.151
CONVERTER HARDWARE, #/FT.SQ? STACK-------?.16
CONVERTER LIFE, ACTIVATIONS[PLATES/H'DWR] ?1,1

          CELL

O.C.VOLTS, VOLTS/CELL-------------------?2.2
CELL POLARIZATION DATA
DATA PT    I,ASF   V,VOLTS
-------    -----   -------
 1      ?   0.166      1.35

INPUT DATA NOT IN CORRECT FORMAT.  RETYPE  IT.
?
                0.166,   1.35
 2      ?       0.333,   0.48
THEO ANODE CONSUMPTION, #/AHR-----------?.00603
THEO CATHODE CONSUPT'N, #/AHR-----------?0
THEO ELECTROLYTE CONSUM., #/AHR-------?0
EXCESS ELECTROLYTE, NO.  STOICS----------?0
EXCESS ELECTROLYTE RECOVERED/ACTIVATION,0/0--?0
WEIGHT OF REACTANT STOREAGE,#/AHR AT 1AHR-?.002
ESTIMATED UTILIZATION, P.C.  THEO/AHR
CATHODE/ANODE/ELECTROLYTE---------------?100,50,100

          MISSION

POWER, WATTS----------------------------?100
CAPACITY, WATT.HOURS-------------------?1000

RATE,HRS       V/CELL      I,ASF          WT.LBS         WH/LB
--------       ------      -----          ------         -----
2              1.1         0.21429        349.782        2.85892
1.66667        1.09        0.216216       416.538        2.40074
1.42857        1.09        0.216216       483.252        2.06932
1.25           1.09        0.216216       549.966        1.8183
1.11111        1.09        0.216216       616.68         1.62159
1              1.09        0.216216       683.394        1.46329
CORRECTED UTILIZATION, THEO/AHOUR
CATHODE/ANODE/ELECTROLYTE ---------------?100,52,100
```

Table 10

ENERGY DENSITIES FOR LITHIUM-CUPRIC SULFIDE CELL SYSTEM WATTHOURS PER POUND - A(1

	Power(2					
Capacity (Watthours)	100 Watts a	b	200 Watts a	b	300 Watts a	b
1,000	2.8	1.4	1.5	0.7	0.59	0.30
10,000	22.7	12.8	12.8	6.9	5.6	2.9
50,000	73.7	48.4	46.5	28.3	23.1	13.0
100,000	112.7	79.3	76.3	49.6	39.7	23.7
200,000	144.2	110.8	113.1	79.5	65.4	41.6
500,000	150.5	128.9	149.5	118.2	113.4	79.7

1) Using isopropylamine electrolyte data and no recovery of electrolyte.
2) Column a is for 5 activations, column b for 10 activations assuming separate units for each activation.

Table 11

ENERGY DENSITIES FOR LITHIUM-CUPRIC SULFIDE CELL SYSTEM WATTHOURS PER POUND - B(1

	Power(2					
Capacity (Watthours	100 Watts a	b	200 Watts a	b	300 Watts a	b
1,000	10.7	9.4	5.9	5.1	2.5	2.1
10,000	57.1	51.9	38.4	34.3	19.9	17.6
50,000	132.4	124.0	96.7	89.3	57.3	52.0
100,000	180.0	170.5	139.8	130.6	87.1	80.1
200,000	182.7	175.7	180.8	171.2	124.6	116.0
500,000	182.4	177.9	200.9	193.7	181.3	171.6

1) Assuming 100 percent recovery of electrolyte from activated cell at no cost in auxiliary equipment. Isopropylamine electrolyte parameters used.

to store, transport, and clean the electrolyte is taken as zero. The cell energy density is improved considerably in some missions, but, even with the optimistic assumptions made, the improvement is not enough to bring the energy density above that for the other systems studied. For this reason, no further detailed analysis was done on this system.

In Table 10, the lower figures for energy density for ten activations (column "b") compared with the figures for five activations (column a) show the effect of the weight of electrolyte used to activate the cells. In Table 11, where this variable has been removed, the much smaller differences shown result from extra casing, plate material, etc. The effect of the high internal resistance is shown by the decrease in the energy density values going from 100 to 500 watt output with the same total energy. This decrease reflects the effect of increased discharge rate and, to some extent, lower utilization efficiency. The effect of high internal resistance is also shown by the increase in energy density with increase in system capacity.

For a given discharge rate, an increase in capacity requires an increase in overall size and thus of the electrode area; this latter requirement decreases the current density needed to obtain the rated output with consequent lower losses caused by the resistance. Some of the increase in energy density with capacity is caused by the greater efficiency of utilization of the container weight, cell casing weight, etc. The weight of these items goes up as the square of the system dimensions, while the volume goes up as the cube. The very low energy density at the 1000 watthour capacity results from a combination of high current densities, inefficient use of the cell casing, containers, etc and the relatively large fixed weight assumed (5 pounds) for switches, etc.

LITHIUM-SELENIUM CELL SYSTEM

Basic System Characteristics

Table 12 gives a summary of the cell system. This system employs a molten salt electrolyte and operates at an elevated temperature. For this study, the heat needed to bring the system to operating temperature is supplied from a pyrotechnic source. Ignition of this source constitutes activation of the system. Since the weight of the heat material required for activation is large, it is obvious that only that part of the power supply needed should be activated (i.e. heated) per activation; otherwise an excessive weight of heat material will be necessary. This calls for a design in which n batteries are provided for n activations.

Data for the cell systems were supplied by Dr. E. J. Cairns of the Argonne National Laboratory, where the system is under intensive investigation. These data are based on results of experiments on small cells at relatively short operating times. Extrapolation to longer running times and for larger units was made because there was no indication of difficulties in so doing. In addition to personal communications with Dr. Cairns and Dr. H. Shimotake, the data used in the analysis were taken from References 5, 6, 7, 8, and 9.

Table 12

LITHIUM-SELENIUM CELL DATA

Anode	Lithium
Cathode	Selenium
Electrolyte	Eutectic LiF, LiCl, LiI immobilized in powdered $LiAlO_2$, Melting point of eutectic is 614°K
Discharge	One-step
Open-circuit Voltage (Theory)	2.6 volts
Open-circuit Voltage (Actual)	2.4 volts
Theoretical Energy Density(1	685 watthours per pound
Status of Development	Experimental

1) For reactants only and theoretical open circuit voltage

Data on the heat source were supplied in a personal communication by Dr. R. Walker of the University of Florida. The heat source is based on a thermite-type reaction; a review of such reactions has been made by Bowen (Ref. 10). Results of calculations made in this study show that it is more economical to supply heat from this source than to use the cell itself for heating after it is brought up to the minimum operating temperature.

Because the system operates at an elevated temperature, the effects of changes in ambient conditions are small and, as a first approximation, can be ignored in making the analysis. However, control of heat losses is necessary. This was done in the study by assuming that the battery was surrounded by reflective heat shields. Data for the probable rate of heat losses were supplied by staff members of the General Electric Research and Development Center; the assumptions made were that the operating temperature was 375°C (648°K), and the heat sink was deep space at 0°K. The actual losses in practice would be smaller than the values used in the study.

System Analysis

The lithium-selenium system is readily adapted to reserve battery design, since the activation is by heating to operating temperature, 375° C (648° K). Arrangement of the cells and the heat source material has not yet been determined, although it is possible to calculate the necessary weight. The activated life is shortened by heat losses, but self-discharge rates are very low with a reasonably thick electrolyte, as called for in the basic design.

The cell reaction is:

$$2Li + Se \rightarrow Li_2Se \qquad E^\circ = 2.60 \text{ volts} \qquad (1)$$

This reaction can be carried out up to consumption of 80 percent of the selenium. The electrode materials are molten at the operating temperature, which contributes to the low internal resistance. However, the lithium selenide formed is not molten at the cell temperature and tends to block the cell discharge reaction, hence the limit on selenium utilization.

Both of the cell electrodes use pure iron for the current collectors. It has been found that the resistance of molten selenium is too high to carry the large currents, hence a relatively large amount of collector (30 weight percent) is used in this electrode. The presently favored design is an iron cup filled with layers of iron mesh or wires welded to the cup walls and bottom. The molten selenium is held in the cup. An iron sinter could also be used and is proposed for the space unit; no tests on such electrodes have been made to date.

The selenium wets the iron, and a sintered structure could hold the selenium in place at zero "g". It should be noted that operation of the cell during acceleration or shock is not anticipated. The design for the lithium electrode is similar although a smaller amount of iron is used--20 weight percent of the lithium.

The cell electrolyte is the eutectic mixture of 11.7 mole percent lithium fluoride, 29.1 mole percent lithium chloride, and 59.2 mole percent lithium iodide and has a melting point of 614°K. This is made into a paste by mixing 50-50 by weight with a lithium aluminate powder to form the electrolyte used. In the study, a volume of 0.1 cubic centimeter was used per square centimeter of electrode surface. The electrolyte has a weight of 0.30 gram per square centimeter.

Table 13 gives the design characteristics of the lithium-selenium cell as reported by the Argonne National Laboratory. The discharge curve for the 0.1 centimeter electrolyte is given in Figure 3. The enormous current density is the most striking feature of the system, reflecting the small internal cell resistance. Pure iron appears to be suitable for the collectors,

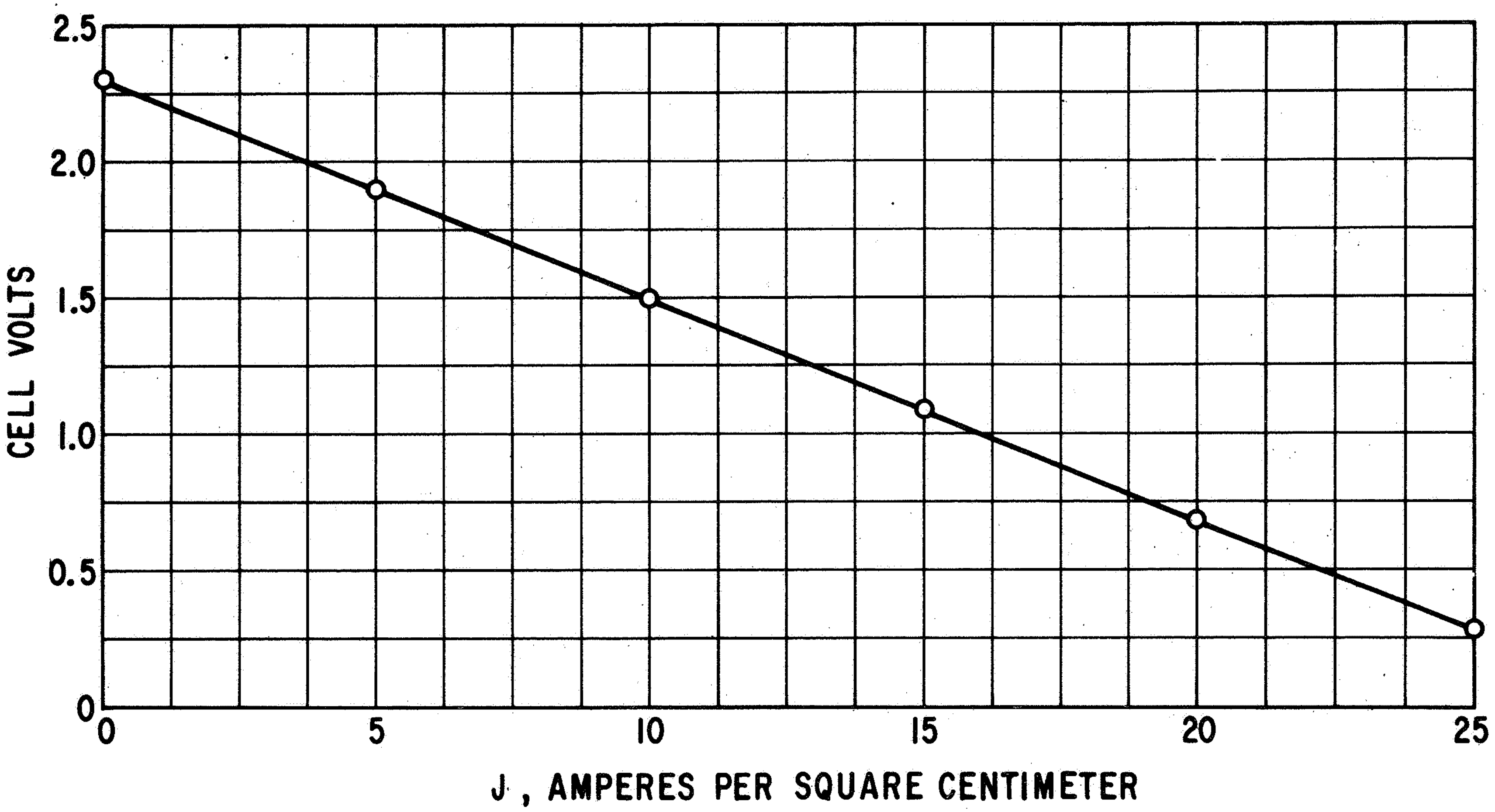

Figure 3. Lithium-selenium Cell (375°C)

partion, housing, etc. A relatively large collector is used to accommodate the large currents.

Table 13

LITHIUM-SELENIUM CELL DESIGN DATA(1

Open Circuit Voltage	2.3 volts
Short Circuit Current Density	
Electrolyte Thickness 0.5 cm	11 amps/cm^2
Electrolyte Thickness 0.1 cm	28 amps/cm^2 (2
Cathode Alloy, fully discharged	
Composition Atom Percent	60%Li
Density	3.3 g/cm^3
Anode Metal Density	0.53 g/cm^3
Cell Partition Thickness	0.1 cm
Density of Housing (Framing Electrolyte)	7.8 g/cm^3
Density of Paste Electrolyte	3.0 g/cm^3
Weight Allowance for Framing, Terminals, etc. as a Percentage of Electrolyte and Partition Weight	50%

1) From Argonne National Laboratory Data
2) Calculated from resistance data on electrolyte. Data for 0.5 centimeter thickness is an experimental value.

The fully discharged alloy composition of 60 atom percent lithium corresponds to 80 percent (by weight) utilization of the selenium. This effiiciency can be increased somewhat for lower drain rates, but this may offer problems in making contact with the current collectors, since the composition corresponding to full utilization (Li_2Se) has a very high melting point. A peculiarity of the cell design is that all of the active components are liquid at the operating temperature, thus giving good contact with each other.

A fundamental problem not solved to date is what material should be used as the gasket seal for the cell. At present, the paste electrolyte serves satisfactorily, but there is considerable doubt of its being adequate for the longer operating times (1000 hours). Since the seal is not thermally cycled, it would appear that a self-baking composition could be used.

The thermal capacity for the system was calculated from equations for the heat capacities of the various components and integrating these equations over the temperature range of 253°K to 648°K (- 20°C to 425°C). In the calculations, the latent heats of fusion were included as appropriate. Data on heat capacities for phases for which there were no experimental data were estimated using the limiting value of 7.50 calories per degree per gram-equivalent. The results were 6300 calories per equivalent weight of active materials for the cell (this included an allowance for the less than 100 percent utilization of active materials, weight of the current collectors, etc.); 72.6 calories per square centimeter for the separator and the partitions; and 150 calories per square centimeter for the end plates.

The thermal losses from the cell were assumed to be by radiation. Assuming a 650°K operating temperature, a reflective shield around the cell, one or more reflecting shields spaced approximately one centimeter from the previous one, and radiation into deep space, a value of $0.017/(N-1)$ watts per square centimeter second was obtained for N shields ($N = 2$ minimum). The shields were assumed to be of thin, ribbed construction with polished gold faces. No correction for progressive cooling of the shields, nor of "warm" sink temperatures was made. Calculations on the effect of shielding using up to six shields were made. For the longer operation times, six shields gave the best energy density; even more shields might be worthwhile.

In calculating the thermal losses, no allowance was made for the I^2R and $T\Delta S$ losses arising from cell discharge, as these are known to be relatively small. Estimates of the $T\Delta S$ term were close to zero, but only approximate methods could be used because of the lack of data. Attempts to incorporate a correction term in the computer program to allow for the I^2R losses failed; this must have been the result of faulty technique in the programming and derivations. The system equations failed to converge to a value for V when all self-heating terms were included.

Figure 4 gives a view of the proposed design. This design is wholly tentative and should not be construed as being more than an initial concept for the power supply for a space mission. Only two heat shields are shown for simplicity.

The heat supply is a critical part of the system. At present, a pyrotechnic heat source is called for. The requirements are: high specific heat output, zero gassing, and long-term storage stability. In addition, a relatively slow burning rate is desirable. The zero gassing requirement is met by using the reaction of active metals with oxides or salts of oxy-acids. In these, oxygen is transferred in the reaction to the active metal. The generic name is "thermite;" this is from the name given to the first reaction of the type studied, e.g., the reaction of iron oxide with aluminum:

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3 \qquad (2)$$

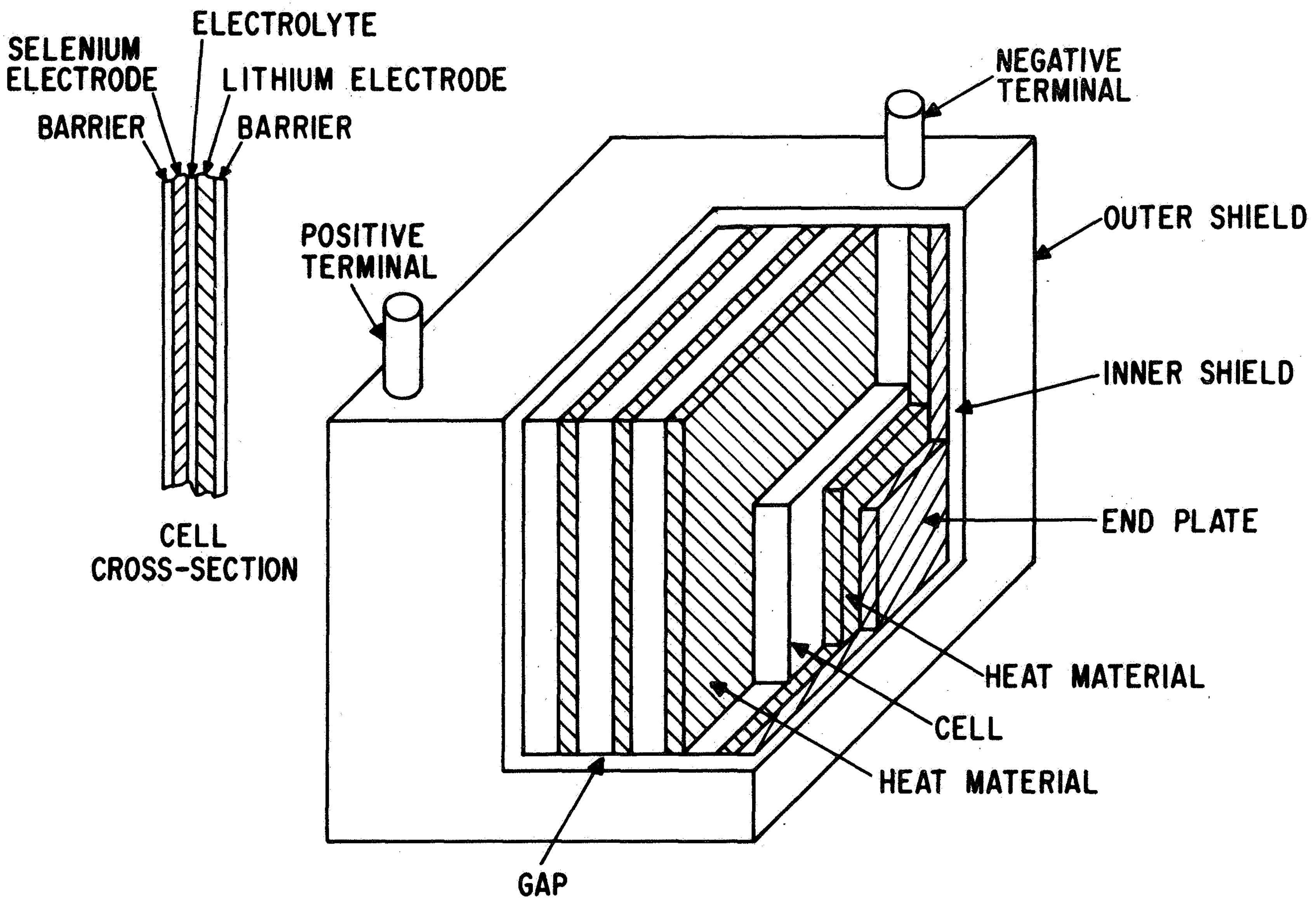

Figure 4. Lithium-selenium Power Supply

This reaction has had widespread use for commercial (welding, filling, etc.) and military (incendiary bombs and antitank weapons) applications; and, surprisingly, it has one of the highest specific heat outputs obtainable from a thermite reaction. Table 14 gives a few examples of possible thermite reactions known; many more have been studied. This table was supplied by Dr. R. W. Walker, University of Florida. In addition to the total amount of heat, the final temperature rise and the rate of reaction are also critical. Thus, the reaction between iron oxide and aluminum results in a very high temperature, well above the melting point of iron; and the reaction is so fast that little heat can be piped away during the reaction time.

The recommended source of heat is a mixture of boron and vanadium pentoxide, this has a flow burning rate (one of the slowest known for pyrotechnic applications) and a high capacity. Studies on its characteristics have been completed recently by Dr. Walker's group. The theoretical heat calculated from the assumed reactions

$$2B + V_2O_5 \rightarrow 2B_2O_3 + V_2O_3 \qquad (3)$$

$$2B + V_2O_3 \rightarrow B_2O_3 + 2V \qquad (4)$$

is about 550 calories per gram. This is found experimentally to be very low by at least 325 calories per gram. The "hottest" mix is 28 weight percent boron, giving about 900 calories per gram total output. A correction for delivery of the heat at 650°K instead of 300°K is needed; this correction reduces the available heat to 748 calories per gram; and this corrected value is the one used in the computer runs. The total amount of gassing is unknown and will have to be determined. This gassing arises from water, etc. held by the reactants and should be reducible to a low value.

System Calculations

The equation programmed into the computer for calculating the minimum weight is:

$$S = \frac{Q}{V}\left[W_1 + \left(a + b\,\frac{Q}{p}\right)\cdot\left(\frac{V}{Q}\right)^{1/3}\right] + \frac{nP}{VJ}\left(W_3 + \frac{V}{E}\cdot W_5\right) + W_7 \qquad (5)$$

Where a and b are heat shield parameters, and the remaining symbols have the meaning defined in Table 2. Table 15 gives the parameter calculations and assignments. The weight of the heating material has been added to the corresponding weights for the chemical or structural elements. The heat material used to compensate for the heat losses (assuming $T\Delta S + I^2R = 0$) is a function of the number of heat shields and is presented as the parameter

$$W_4 = a + b\,\frac{Q}{P}\,.$$

Table 14

HEAT OUTPUT FOR THERMITE REACTIONS(1

Fuel	Oxidant	Calories per Gram
Al	Fe_2O_3	950
Al	$CaCrO_4$	855
B	V_2O_5	550
Ca	K_2CrO_4	465
Ca	$K_2Cr_2O_7$	785
Ca	$BaCrO_4$	495
Ca	$CaCrO_4$	855
Ca	$PbCrO_4$	515
Li	$CaCrO_4$	980
Mg	K_2CrO_4	460
Mg	$BaCrO_4$	490
Mg	$CaCrO_4$	895
Mg	V_2O_5	1025
Zn	$CaCrO_4$	320
Zr	$CaCrO_4$	670
Zr	$BaCrO_4$	500
Zr	Ag_2CrO_4	1000

1) Taken from data supplied by Dr. R. W. Walker, University of Florida, Gainesville, Florida. Heat outputs are theoretical values; actual values tend to be greater because of secondary reactions occurring after the main reaction.

Table 15

LITHIUM-SELENIUM SYSTEM PARAMETERS

W_1 = Reactant Weight plus Thermal Weight

$$= \frac{73.6}{26.8} \times \frac{1}{454} + \frac{6300}{748 \times 454 \times 26.8}$$

= 0.00678 pounds per ampere-hour

W_2 = Container Weight = 0

W_3 = Converter Weight + Thermal Weight

$$= 1.08 \times \frac{929}{454} + \frac{72.6}{74.8} \times \frac{929}{454}$$

= 2.41 pounds per square foot

W_4 = Shield and Thermal loss Weight = $a + b\,\frac{Q}{p}$

W_5 = End plate plus Thermal Weight

$$= 3.12 \times \frac{929}{454} + \frac{150}{748} \times \frac{929}{454}$$

= 6.81 pounds per square foot

W_6 = Weight Power Conditioning = 0

W_7 = Fixed Weight (Switches, buses, and connectors) = 10 pounds

J = 21,300 - 9,290 Volts amperes per square foot

a = Shield weight pounds per ampere-hour $^{2/3}$	b = Thermal loss coefficient pounds per hour x ampere $^{2/3}$	Number of Shields
2.83×10^{-3}	2.90×10^{-4}	2
3.24×10^{-3}	1.45×10^{-4}	3
3.66×10^{-3}	9.65×10^{-5}	4
4.15×10^{-3}	7.25×10^{-5}	5
4.55×10^{-3}	5.80×10^{-5}	6

The calculation of parameter a was as follows:

$$a = k_x \left(\frac{w_a}{d_a}\right)^{2/3} \times (K + (N-1)\, W_s) \times F_1 .$$

where

k_x = proportionality factor for relating area to $(\text{volume})^{2/3}$ (for cubes $k_x = 6$)

$\frac{w_a}{d_a}$ = volume of active materials for one ampere-hour

K = specific weight of first heat shield and insulation, 0.17 gram per square centimeter

N = number of heat shields, $N \geq 2$

W_s = specific weight of second and subsequent shields, 0.03 gram per square centimeter

F_1 = conversion factor, gram per square centimeter to pounds/square feet = 929/454 = 2.05 square centimeter/grams × pounds/square feet

$\frac{w_a}{d_a}$ = 28.0 cubic centimeter per equivalent; 28.0/26.8 = 1.05 cubic centimeter per ampere-hour

therefore

$$k_x\left(\frac{w_a}{d_a}\right)^{2/3} = 6 \times 1.05^{2/3} \times 1/929 = 6.90 \times 10^{-3}$$ square foot per per ampere-hour $^{2/3}$

For $N = 2$

$$a = 6.90\times10^{-3} \times 0.20 \times 929/454 = 2.83 \times 10^{-3}$$ pounds per $(\text{ampere-hour})^{2/3}$

$$b = k_x\left(\frac{w_a}{d_a}\right)^{2/3} \times \frac{L}{w_q} \times \frac{Q}{P} \times F_1 \times F_2$$

where

F_2 = seconds per hour

L = heat loss coefficient = $0.017/(N-1)$ calorie per second × square centimeter

W_q = specific heat content of heat material, 748 calorie per gram

$\frac{Q}{P}$ = time of operation in hours (total system)

$$b = 6.90 \times 10^{-3} \times 0.017/748 \times Q/P \times 2.05 \times 3600$$
$$= 2.90 \times 10^{-4} \times \frac{Q}{P} \quad \text{pound per (ampere hour)}^{2/3}$$

In the computer equation, the factor (a + b Q/P) must be multiplied by $(Q/V)^{-1/3}$ to correct for use of Q/V ahead of the expression containing the factor. This is expressed as $(V/Q)^{1/3}$ in the program.

Table 16 gives the computer program in BASIC. The symbols used in this table are not the ones used in the equation, because of the computer input limitations. Table 17 gives a selected set of results, illustrating the effects of various mission variables on the energy density, particularly the number of shields used. The effect of the number of shields on energy density is about as expected, based on a consideration that the heat loss varies with both the time of operation and the number of shields. For a given power output and capacity, the energy density increases with the number of shields, except for the lowest capacity, where the necessary shield weight exceeds the saving in the heat material weight.

As for the lithium-cupric sulfide system, the fixed weight and the necessary increase in current density for short discharge times make this set of missions have a low energy density, and the decrease with power output is normal. The decrease in energy density with the number of activations is, in all cases, normal. However, heat losses override the normal increase in energy density with increase in capacity, because the increase in capacity means a longer discharge time and consequently more losses. The fact that the energy density reaches a maximum in the 50,000 to 100,000 watt-hour range, indicates that the use of more shields would probably be profitable for longer time missions; this can be worked out in advanced design studies. It is obvious that the use of at least six shields is needed for all but the smaller capacities.

Table 18 gives a complete run of the calculations, using the program of Table 16 and the parameters of Table 15. Only the results for six shields are given. The same general observations on the variation in energy density with the mission for the previous table can be made with Table 18. The total weight values for a 1000-ampere-hour capacity are notable in that 10 pounds of the total is the fixed weight, leaving less than 5 pounds for the battery. In Table 18, the number of activations is indicated indirectly in the first column (rate, hours); the rates are calculated from the expression Q/nP, where n varies from 5 to 10.

The generally high energy densities compared with the other systems, plus the prospect of improving the thermal balance, and the relatively simple method for activation have led to the recommendation that this system be used as the basis for further study of multiple reserve power sources. This recommendation is made with the full knowledge that many practical problems have to be solved, such as gaskets, thermal balance, electrode construction, corrosion, gas evolution, heat source distribution, etc. However, the energy densities appear to be realistic and are obtained without gross extrapolation of present data, except operating time.

Table 16

ENERGY DENSITY COMPARISON LITHIUM-SELENIUM CELLS

```
MRPS2      16:05    AUGUST 13, 1968

40 PRINT "FIXED WT. W, LBS.---------------";
45 INPUT W
50 PRINT "SPECIFIC REACTANT CONSUMPTION,#/A.HR---";
60 INPUT W1
70 PRINT "CONVERTER"
75 PRINT "PLATES AND FRAMES, LBS/FT.SQ.----------";
80 INPUT W6
85 PRINT "CONVERTER HD WARE, LBS/FT.SQ.STACK-----";
90 INPUT W7
130 PRINT "MISSIONPOWER LEVELS"
132 PRINT "NO. OF POWER LEVELS"
133 INPUT L1
135 PRINT "LEVEL    WATTS"
140 FOR I=1 TO L1
145 PRINTI;
150 INPUT P(I)
160 NEXT I
170 PRINT "MISSION CAPACITIES"
175 PRINT "NO. OF CAPACITY LEVELS--";
180 INPUT L2
190 PRINT "LEVEL   WATT HOURS"
195 FOR M=1 TO L2
200 PRINTM;
205 INPUT Q(M)
210 NEXT M
211  PRINT "THERMAL SHIELDING"
212  PRINT "A,LBS/AHR------------------";
213  INPUT A
214  IF A=0 THEN 450
215  PRINT "B,LBS/AHRSQ----------------";
216  INPUT B
217  PRINT
220 PRINT
230 FOR I=1 TO L1
235 FOR M=1 TO L2
240 PRINT "POWER,WATTS--------------",P(I)
250 PRINT "CAPACITY,WHOURS----------",Q(M)
255 PRINT
260 PRINT "RATE,HRS","V.CELL","I,ASF","WT.LBS","WH/LB"
280 FOR N=5 TO 10
285 LET X=0
290 LET T=Q(M)/(N*P(I))
300  LET V=2.28
305  LET J=  2.12E+4  - (9.290E+3)*V
310   LETS1=Q(M)/V*( W1 +(A+B*Q(M)/P(I))*(V/Q(M))↑0.333)
320 LET S2=N/V*P(I)/J*(W6+W7*V/28)
330 LET S3=W
340 LET S=S1+S2+S3
345 IF X=0 THEN 355
350 IF S>=X THEN 380
355 LET X=S
357 IF V<=1.20 THEN 380
360 LET V=V-.01
370 GO TO 305
380 PRINT T,V,J,X,Q(M)/X
390     NEXT N
400 PRINT
405 PRINT
410 NEXT M
420 NEXT I
430  GO TO 211
450 END
```

Table 17

LITHIUM-SELENIUM CELL CALCULATION SUMMARY(1

No Shields	100 Watts		200 Watts		500 Watts	
	5(2	10	5	10	5	10
	1,000 Watthours Capacity					
2	75.2	74.2	74.6	73.0	72.5	69.9
3	75.5	74.4	74.6	73.0	72.5	69.8
6	75.3	74.2	74.3	72.7	72.1	69.4
	10,000 Watthours Capacity					
2	227.6	224.6	241.9	237.3	246.6	238.9
4	244.6	241.3	251.0	246.0	250.0	242.0
6	254.3	250.7	254.8	249.8	250.2	242.2
	50,000 Watthours Capacity					
2	219.9	211.6	262.9	260.4	303.1	297.9
4	264.3	262.5	298.6	295.4	320.5	314.8
6	307.2	304.9	323.2	319.7	330.0	324.1
	100,000 Watthours Capacity					
2	172.1	176.4	237.6	236.0	296.8	293.4
4	238.4	237.3	287.0	285.0	324.6	320.6
6	299.2	237.3	326.3	323.7	342.3	335.9
	200,000 Watthours Capacity					
2	137.3	137.0	200.4	199.6	275.7	273.5
4	200.9	200.3	260.6	259.4	315.7	313.0
6	276.9	275.7	316.5	314.9	344.5	341.4
	500,000 Watthours Capacity					
2	89.8	89.7	145.3	145.1	230.2	229.2
4	145.4	145.3	210.3	209.8	286.1	284.8
6	230.0	229.7	286.2	285.2	333.9	332.1

1) Watthours per pound of optimum systems for each mission as indicated. Computed using the program shown in Table 18.

2) Number of activations.

Table 18

LITHIUM-SELENIUM CELL CALCULATIONS

```
FIXED WT. W, LBS.---------------?10
SPECIFIC REACTANT CONSUMPTION,#/A.HR---?6.78E-3
CONVERTER
PLATES AND FRAMES, LBS/FT.SQ.----------?2.41
CONVERTER HD WARE, LBS/FT.SQ.STACK-----?6.81
MISSIONPOWER LEVELS
NO. OF POWER LEVELS
?3
LEVEL     WATTS
 1     ?    100
 2     ?    200
 3     ?    500
MISSION CAPACITIES
NO. OF CAPACITY LEVELS--?6
LEVEL    WATT HOURS
 1     ?    1000
 2     ?    1E+4
 3     ?    5E+4
 4     ?    1E+5
 5     ?    2E+5
 6     ?    5E+5
THERMAL SHIELDING
A,LBS/AHR-----------------?4.55E-3
B,LBS/AHRSQ---------------?5.80E-5


POWER,WATTS-------------         100
CAPACITY,WHOURS---------         1000

RATE,HRS       V.CELL        I,ASF          WT.LBS          WH/LB
--------       ------        -----          ------          -----
 2              2.07          1969.7         13.9486         71.692
 1.66667        2.05          2155.5         14.0198         71.3274
 1.42857        2.04          2248.4         14.0866         70.9893
 1.25           2.02          2434.2         14.1493         70.6749
 1.11111        2.01          2527.1         14.2092         70.3771
 1              1.99          2712.9         14.2666         70.0938

POWER,WATTS-------------         100
CAPACITY,WHOURS---------         10000

RATE,HRS       V.CELL        I,ASF          WT.LBS          WH/LB
--------       ------        -----          ------          -----
 20             2.2           762.           44.5148         224.644
 16.6667        2.2           762.           44.7141         223.643
 14.2857        2.19          854.9          44.896          222.737
 12.5           2.19          854.9          45.0716         221.869
 11.1111        2.18          947.8          45.2302         221.091
 10             2.18          947.8          45.3873         220.326

POWER,WATTS-------------         100
CAPACITY,WHOURS---------         50000

RATE,HRS       V.CELL        I,ASF          WT.LBS          WH/LB
--------       ------        -----          ------          -----
 100            2.24          390.4          189.483         263.876
 83.3333        2.24          390.4          189.925         263.262
 71.4286        2.24          390.4          190.366         262.651
 62.5           2.23          483.3          190.729         262.152
 55.5556        2.23          483.3          191.067         261.689
 50             2.23          483.3          191.405         261.227

POWER,WATTS-------------         100
CAPACITY,WHOURS---------         100000

RATE,HRS       V.CELL        I,ASF          WT.LBS          WH/LB
--------       ------        -----          ------          -----
 200            2.25          297.5          391.731         255.277
 166.667        2.25          297.5          392.371         254.861
 142.857        2.25          297.5          393.011         254.446
 125            2.24          390.4          393.631         254.045
 111.111        2.24          390.4          394.072         253.761
 100            2.24          390.4          394.514         253.476
```

Table 18 (Cont'd)

LITHIUM-SELENIUM CELL CALCULATIONS

```
POWER,WATTS-------------          100
CAPACITY,WHOURS---------          200000

RATE,HRS          V.CELL          I,ASF          WT.LBS          WH/LB
--------          ------          -----          ------          -----
 400               2.26            204.6           852.797         234.522
 333.333           2.26            204.6           853.965         234.202
 285.714           2.25            297.5           854.786         233.977
 250               2.25            297.5           855.426         233.802
 222.222           2.25            297.5           856.066         233.627
 200               2.25            297.5           856.706         233.452

POWER,WATTS-------------          100
CAPACITY,WHOURS---------          500000

RATE,HRS          V.CELL          I,ASF          WT.LBS          WH/LB
--------          ------          -----          ------          -----
 1000              2.26            204.6           2587.94         193.204
 833.333           2.26            204.6           2589.11         193.117
 714.286           2.26            204.6           2590.27         193.03
 625               2.26            204.6           2591.44         192.943
 555.556           2.26            204.6           2592.61         192.856
 500               2.26            204.6           2593.78         192.769


POWER,WATTS-------------          200
CAPACITY,WHOURS---------          1000

RATE,HRS          V.CELL          I,ASF          WT.LBS          WH/LB
--------          ------          -----          ------          -----
 1                 1.99            2712.9          14.2483         70.1839
 .833333           1.97            2898.7          14.3564         69.6553
 .714286           1.95            3084.5          14.4581         69.1654
 .625              1.93            3270.3          14.5547         68.7065
 .555556           1.92            3363.2          14.647          68.2734
 .5                1.9             3549.           14.7357         67.8623

POWER,WATTS-------------          200
CAPACITY,WHOURS---------          10000

RATE,HRS          V.CELL          I.ASF          WT.LBS          WH/LB
--------          ------          -----          ------          -----
 10                2.17            1040.7          44.5865         224.283
 8.33333           2.17            1040.7          44.8711         222.861
 7.14286           2.16            1133.6          45.1343         221.561
 6.25              2.15            1226.5          45.3822         220.351
 5.55556           2.14            1319.4          45.6186         219.209
 5                 2.14            1319.4          45.841          218.145

POWER,WATTS-------------          200
CAPACITY,WHOURS---------          50000

RATE,HRS          V.CELL          I,ASF          WT.LBS          WH/LB
--------          ------          -----          ------          -----
 50                2.23            483.3           179.871         277.977
 41.6667           2.22            576.2           180.503         277.003
 35.7143           2.22            576.2           181.051         276.165
 31.25             2.22            576.2           181.599         275.332
 27.7778           2.21            669.1           182.097         274.578
 25                2.21            669.1           182.559         273.885

POWER,WATTS-------------          200
CAPACITY,WHOURS---------          100000

RATE,HRS          V.CELL          I,ASF          WT.LBS          WH/LB
--------          ------          -----          ------          -----
 100               2.24            390.4           357.997         279.332
 83.3333           2.24            390.4           358.881         278.644
 71.4286           2.24            390.4           359.765         277.96
 62.5              2.23            483.3           360.457         277.426
 55.5556           2.23            483.3           361.132         276.907
 50                2.23            483.3           361.808         276.39

POWER,WATTS-------------          200
CAPACITY,WHOURS---------          200000

RATE,HRS          V.CELL          I.ASF          WT.LBS          WH/LB
--------          ------          -----          ------          -----
 200               2.25            297.5           741.089         269.873
 166.667           2.25            297.5           742.369         269.408
 142.857           2.25            297.5           743.649         268.944
 125               2.24            390.4           744.792         268.531
 111.111           2.24            390.4           745.676         268.213
 100               2.24            390.4           746.56          267.896
```

Table 18 (Cont'd)

LITHIUM-SELENIUM CELL CALCULATIONS

```
POWER,WATTS-------------       200
CAPACITY,WHOURS---------       500000

RATE,HRS       V.CELL          I,ASF           WT.LBS          WH/LB
--------       ------          -----           ------          -----
 500            2.26           204.6           2062.76         242.394
 416.667        2.26           204.6           2065.09         242.12
 357.143        2.26           204.6           2067.43         241.846
 312.5          2.25           297.5           2069.54         241.6
 277.778        2.25           297.5           2070.82         241.45
 250            2.25           297.5           2072.1          241.301

POWER,WATTS-------------       500
CAPACITY,WHOURS---------       1000

RATE,HRS       V.CELL          I,ASF           WT.LBS          WH/LB
--------       ------          -----           ------          -----
 .4             1.87           3827.7           14.9342         66.9602
 .333333        1.84           4106.4           15.1307         66.0909
 .285714        1.81           4385.1           15.317          65.2867
 .25            1.79           4570.9           15.4959         64.5333
 .222222        1.76           4849.6           15.6683         63.8233
 .2             1.74           5035.4           15.8355         63.1493

POWER,WATTS-------------       500
CAPACITY,WHOURS---------       10000

RATE,HRS       V.CELL          I,ASF           WT.LBS          WH/LB
--------       ------          -----           ------          -----
 4              2.12           1505.2           45.8699        218.008
 3.33333        2.11           1598.1           46.3421        215.786
 2.85714        2.1            1691.            46.7825        213.755
 2.5            2.09           1783.9           47.1964        211.88
 2.22222        2.08           1876.8           47.5884        210.135
 2              2.07           1969.7           47.962         208.498

POWER,WATTS-------------       500
CAPACITY,WHOURS---------       50000

RATE,HRS       V.CELL          I,ASF           WT.LBS          WH/LB
--------       ------          -----           ------          -----
 20             2.2            762.             176.684        282.991
 16.6667        2.2            762.             177.681        281.404
 14.2857        2.19           854.9            178.572        279.999
 12.5           2.18           947.8            179.439        278.646
 11.1111        2.18           947.8            180.225        277.431
 10             2.17           1040.7           181.003        276.239

POWER,WATTS-------------       500
CAPACITY,WHOURS---------       100000

RATE,HRS       V.CELL          I,ASF           WT.LBS          WH/LB
--------       ------          -----           ------          -----
 40             2.22           576.2            341.342        292.961
 33.3333        2.22           576.2            342.711        291.791
 28.5714        2.21           669.1            343.996        290.701
 25             2.21           669.1            345.149        289.73
 22.2222        2.21           669.1            346.302        288.765
 20             2.2            762.             347.335        287.907

POWER,WATTS-------------       500
CAPACITY,WHOURS---------       200000

RATE,HRS       V.CELL          I,ASF           WT.LBS          WH/LB
--------       ------          -----           ------          -----
 80             2.24           390.4            679.192        294.467
 66.6667        2.23           483.3            681.14         293.625
 57.1429        2.23           483.3            682.829        292.899
 50             2.23           483.3            684.519        292.176
 44.4444        2.23           483.3            686.208        291.457
 40             2.22           576.2            687.581        290.875

POWER,WATTS-------------       500
CAPACITY,WHOURS---------       500000

RATE,HRS       V.CELL          I,ASF           WT.LBS          WH/LB
--------       ------          -----           ------          -----
 200            2.25           297.5            1755.75        284.779
 166.667        2.25           297.5            1758.95        284.261
 142.857        2.25           297.5            1762.15        283.744
 125            2.24           390.4            1764.77        283.324
 111.111        2.24           390.4            1766.97        282.97
 100            2.24           390.4            1769.18        282.616
```

METAL-OXYGEN CELL SYSTEMS

General Cell Characteristics

The metal-oxygen cells studied are the primary zinc-oxygen and aluminum-oxygen cells. The zinc cell uses a potassium hydroxide electrolyte. The oxygen cathode is a thin platinum-catalyzed porous electrode. The aluminum anode is a special alloy which shows substantially less self-discharge on open circuit than do other aluminum alloys, yet it has the capability of providing high current drains. The zinc anode is an amalgamated zinc sheet or sinter. The general cell reaction is

$$O_2 + 2H_2O + 4M \rightarrow 4MOH \qquad (6)$$

where M is an equivalent of the metal. Note that both water and oxygen are consumed.

Table 19 gives the basic characteristics for the two cell types. The oxygen supply is not specified, as its selection is dependent upon a number of considerations discussed in later sections of this report.

Data on the cell systems were taken from internal references on experimental work performed at the General Electric Research and Development Center.

Table 19

METAL-OXYGEN CELL DATA

Anode	Aluminum	Zinc
Cathode	Oxygen	Oxygen
Electrolyte	10% NaC1	45% KOH
Discharge	one-step	one-step
Open Circuit Voltage, (Theory)	2.05 volts	1.80 volts
Open Circuit Volgage, (Actual)	1.60 volts	1.60 volts
Theoretical Energy Density(1	1470 watthours per pound	540 watthours per pound
State of Development	Experimental	Prototype

1) Active materials only at theoretical open-circuit voltage

Cell Anodes

Both aluminum and zinc anodes undergo parasitic or side reactions with water. The rate of this parasitic reaction is a complex function of anode composition, previous heat treatment and work hardening, and electrolyte composition. The use of high-purity aluminum or zinc is generally unsatisfactory, because these have high parasitic rates and passivate readily. For reasonable performance in a cell, an alloy must be used to control both the tendency towards passivation and reduce the parasitic reaction rate to acceptable levels. For zinc, mercury is one of the best alloying agents; in this study the zinc anodes were high-purity zinc (New Jersey Zinc Company, Mix 60) amalgamated with two percent mercury by weight. Little work has been reported on aluminum anode alloys. This study used published data on a proprietary aluminum-tin alloy (with gallium and manganese) from Olin Metals, Incorporated (OML-A6).

Both aluminum and zinc show an increase in the rate of the parasitic reaction with an increase in current density when operated in alkaline or saline electrolytes. This means that the coulombic efficiency of the anode decreases as the current density is increased. Table 20 shows the coulombic efficiency of 74 to 84 percent over the range of discharge current densities shown in the table.

Table 20

COULOMBIC EFFICIENCY (η) OF ALUMINUM ANODES(1

Current Density (milliampere per square centimeter)	Efficiency percent
10	74
20	82
30	84
40	74

1) Determined by measuring rate of hydrogen evolution during discharges at constant current.

In addition to parasitic reaction losses, both types of anodes also show passivation and mechanical losses. The mechanical losses result from intergranular attack that loosens the grains from the main body of the electrode. The losses due to passivation are also a function of the rate of discharge, particularly for zinc. The overall loss rate for zinc is a function of the amount of electrolyte. Table 21 gives the overall loss factor as a function of the discharge rate and the electrolyte quantity; these are experimental values. The magnesium electrode must be operated in a flooded condition.

Table 21

LOSS FACTOR (μ) FOR SLOUGHING AND PASSIVATION(1

Discharge Rate (Hours)	Aluminum and Zinc (Starved)(2	Zinc (Wet)(2	Zinc (Flooded)(2
1	0.30	0.22	0.15
5	0.25	0.18	0.13
10	0.22	0.16	0.11
50	0.16	0.11	0.10
100	0.14	0.09	0.07
200	0.12	0.08	0.05
500	0.09	0.05	0.04
1000	0.06	0.04	0.03

1) Fraction of active material unavailable for cell reaction

2) Electrolyte quantity is defined as follows (For Zinc Electrode Only):

Starved:	Cell has no free electrolyte present, all of the electrolyte is immobilized in the separator or plates.
Wet:	Cell has free electrolyte present, but only enough to immerse the electrodes 0 to 10 percent.
Flooded:	Electrodes are immersed in the electrolyte; the term usually implies a large excess of electrolyte.

For computations, the overall efficiency of utilization is set by dividing the coulombic efficiency, η, of Table 20 by $(1 + \mu)$, where μ is the loss factor from Table 21. Since η is dependent upon the current density, a second approximation in the calculation of the optimum cell operating voltage is often needed.

The cell reaction for aluminum is assumed to be:

$$\begin{aligned} &Al + 1.5\,(1 + x)\,(2 - \eta)\,H_2O + 0.75\,O_2 \rightarrow \\ &\quad Al(OH)_3 + 1.5\,(1 - \eta)H_2 + 1.5x\,(2 - \eta)\,H_2O \end{aligned} \qquad (7)$$

with the production of three Faradays of electricity; where η is the coulombic efficiency, and x is the amount of water required in the cell as the invariant electrolyte. This amount of water is generally expressed in stoichiometric ratios, i. e., the number of equivalents of electrolyte per equivalent of aluminum. An analysis of the specific volumes of the nongaseous constituents of the reaction show that about two equivalents ($x = 2$) of excess water per equivalent of aluminum are required to limit the relative volume change during cell discharge to less than 20 percent. In calculating the weight of the materials, the appropriate correction for sloughing and passivation from Table 21 must be used.

The zinc-oxygen cell reaction is assumed in the calculations to be:

$$Zn + 0.5\,O_2 + 2(1-f)\,KOH = f\,Zn(OH)_2 + (1-f)K_2ZnO_2 + (1-2f)\,H_2 \qquad (8)$$

where f is the fraction of the zinc consumed electrochemically to form zinc hydroxide; the remainder of the zinc is assumed to form zincate. The consumption of electrolyte depends upon the value of f as shown in Table 22. Experimental results show that the zinc cell must have 0. 6 to 1. 0 cubic centimeter of 45 percent potassium hydroxide per ampere-hour above the reaction amount to achieve reasonable zinc consumption. This amount of electrolyte corresponds to the "starved" condition.

Table 22

ZINC CELL ELECTROLYTE CONSUMPTION(1

	Electrolyte Consumption		
f	pounds per ampere-hour	cubic centimeter per ampere-hour	Cell Condition(2
0.0	0.0102	3.10	Flooded
0.5	0.0051	1.60	Wet
1.0	0.0014	0.41	Starved

1) Calculated for 45 percent potassium hydroxide, Sp. G. 1.50.

2) Approximate behavior shown in these electrolytes; e.g., in flooded cells, the tendency is to form zincate rather than hydroxide as the end product.

Table 23 shows the overall anode utilization resulting from the combined inefficiencies and parameter assignments for the 108 missions. In the table, η is the coulombic efficiency and is a function of the current density for aluminum. The value of η for zinc was taken as constant at 80 percent. The correction for anode losses, μ, was taken from a plot of the data for Table 21. The overall utilization is given by $\eta\ /(1+\mu)$.

Figure 5 gives the single cell performance curves used in the calculations. These curves were constructed from reported metal-air cell data, with corrections for operation of the cathode in oxygen rather than air.

Table 23

ANODE EFFICIENCIES

	Mission Parameters(1		Anode Utilization (percent)			
					Zn	
Power (Watts)	Capacity (1000 Watthours)	Discharge Rate(2 (Hours)	Al	Flooded	Wet	Starved
100	1	1-2	$\eta/1.3$	70	66	62
	10	10-20	$\eta/1.22$	73	69	66
	50	50-100	$\eta/1.15$	75	71	70
	100	100-200	$\eta/1.12$	76	73	71
	200	200-400	$\eta/1.09$	77	75	73
	500	400-1000	$\eta/1.06$	78	77	75
200	10	5-10	$\eta/1.24$	72	67	64.5
	50	25-50	$\eta/1.18$	74	70	68
	100	50-100	$\eta/1.15$	75	71	70
	200	100-200	$\eta/1.12$	76	73	71
	500	200-500	$\eta/1.08$	77	75	74
500	10	2-4	$\eta/1.27$	72	67	63
	50	10-20	$\eta/1.22$	73	69	66
	100	20-40	$\eta/1.19$	74	70	67
	200	40-80	$\eta/1.16$	75	71	69
	500	100-200	$\eta/1.12$	76	73	70

1) Each mission is defined by power level, capacity, and number of activations. Number of activations for each power level and capacity is 5 to 10.

2) Time in hours per activation; this is fixed for each mission by the combination of the three primary parameters.

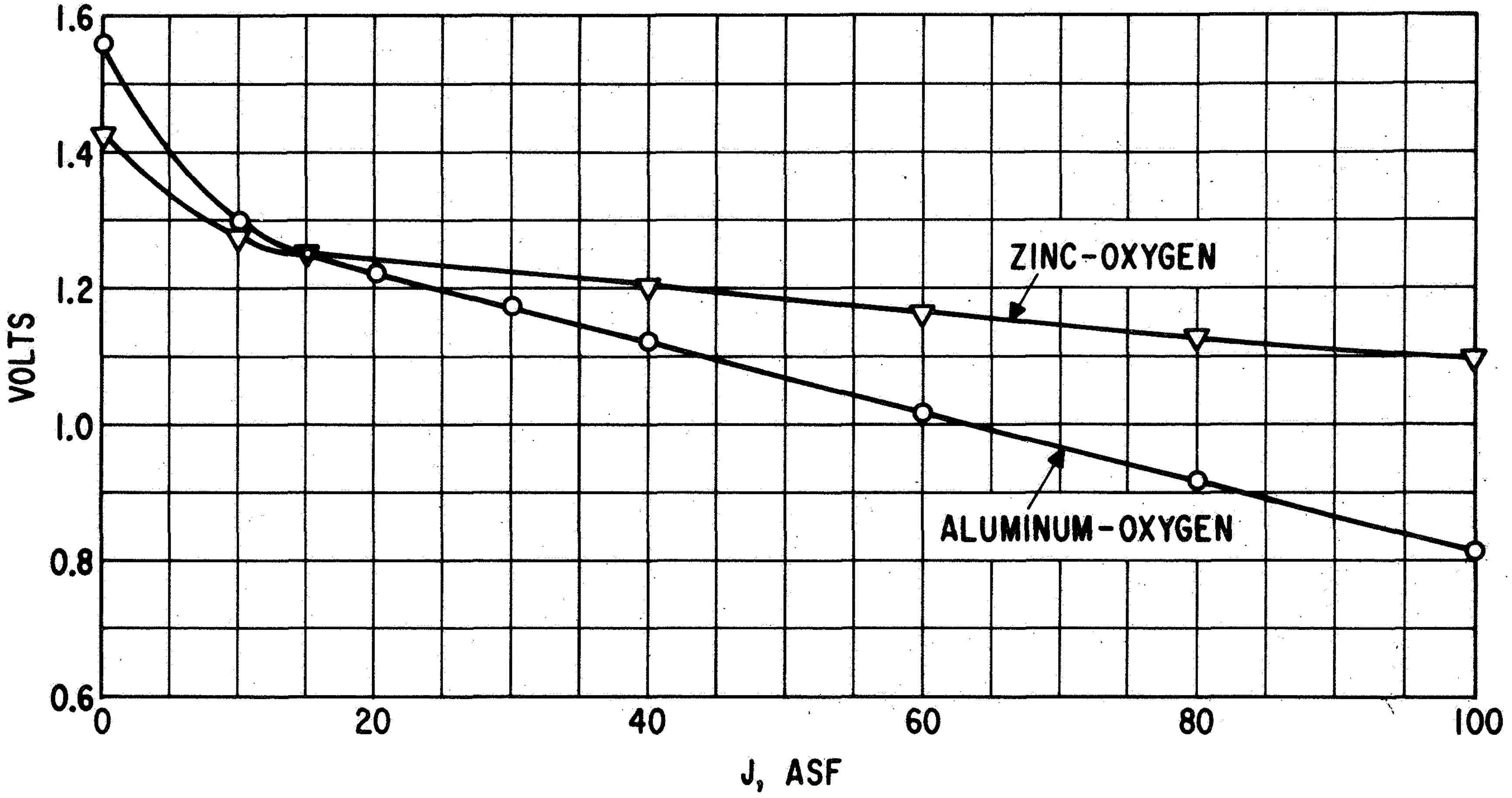

Figure 5. Metal-oxygen Cell Polarization

Oxygen Supply

The method used to store oxygen has a large effect on the system energy density because of the weight and the heat involved with a specific system of storage. Four different types of storage were considered: sodium chlorate candles, compressed oxygen in steel cyclinders, compressed oxygen in filament-wound spheres, and hydrogen peroxide. Any cell reaction water, not supplied by the stored oxygen supply, was assumed to be stored in a separate vessel.

The weight of each vessel was assumed to vary with the weight of the contents as follows:

$$M_{c,j} = K \left(M_j \right)^{2/3} = K \left(\frac{Q}{V} \cdot W_j \right)^{2/3} \qquad (9)$$

where:

K = proportionality constant

$M_{c,j}$ = weight of container for M_j

M_j = weight of oxygen supply

W_j = specific weight of oxygen supply material

Table 24

OXYGEN STORAGE VESSEL DATA

Oxygen Source	Size Factor, K (Pounds $^{1/3}$)	Specific Weight, W_j (Pounds/ampere hour)	Remarks
H_2O_2	0.87	0.0014	90% H_2O_2
O_2 in filament-wound sphere	5.06	0.00066	O_2 at 11,000 PSI
O_2 in steel cylinder	16.2	0.00066	O_2 at 2,000 PSI
Chlorate Candle	3.42	0.00206	NaCl O_3 -Cat.
H_2O(1	0.87	0.00075	H_2O

1) For supplying water to cell reaction or for cooling.

Table 24 gives the pertinent data for the vessels and the specific weights. Only one fully engineered system for generating gaseous oxygen from a chemical source has been found to date. This system is based on the sequential thermal decomposition of sodium chlorate candles contained in a pressure vessel fitted with a suitable pressure regulator. Heat for the pyrolysis is supplied by burning iron chips contained in the candle using the perchlorate as the oxidant. This iron comprises about 25 to 30 percent of the candle weight.

Other pyrolytic sources are known, but have been largely of theoretical interest. These include lithium, sodium, and potassium superoxides (MO_2), peroxides (M_2O_2), perchlorates ($MClO_4$), and chlorates ($MClO_3$). All require heat sources, usually iron or other metal placed in the material. Perchlorates and chlorates benefit from the addition of small amounts of catalysts and combustible binders. Hydrogen peroxide as an oxygen source requires only a catalyst and heat sink, however, considerable heat is evolved on decomposition. The residual water can be used in the cell or for cooling. Compressed oxygen is the simplest to use, but the container weights are large. Cryogenic storage is not allowable because of the long stand times.

The optimum (lowest weight) systems for each of the 108 missions based on aluminum-oxygen cells were computed for each of the oxygen supplies, using the program given in Table 25. The parameter values used are shown, in program format, at the end of Table 25. In the calculation, no provision for heat transfer was made. On this basis, the hydrogen peroxide system is the best of the four with respect to energy density. Table 26 gives a summary of the results.

Heat Transfer

General. In the absence of either a gravitational field or an ambient fluid (both required for natural convection) an additional weight penalty must be imposed on the power source if its operating temperature is to be controlled. The performance debit incurred in heat transfer equipment will, of course, increase with the ambient temperature, as heat must always be rejected from the cell system during its operation. Table 27 lists the possible environmental conditions in which the battery system may have to operate and summaries the corresponding alternative heat transfer mechanisms.

Under the first two conditions listed in Table 27, the energy densities of Table 26 may be assumed without appreciable modification. When radiational heat transfer is feasible (Condition No. 3), the rate of heat generation in the system will be the key factor in determining the system performance debit as additional heat transfer surface area may be required. When the ambient temperature is above the maximum cell operating temperature (Condition No. 4), heat removal from the battery must be achieved by mass transfer (transpiration cooling). Under these conditions, the weight penalty for temperature moderation is related to the product of the heat generation rate and the duration of the discharge. The weight of transpirational fluid, as well as that of its storage vessel, must be included in determining the overall system energy density under these conditions.

Table 25

METAL/OXYGEN CELL SYSTEM PROGRAM

```
MRPS3       9:41   AUG.8,1968

40 PRINT "          ALUMINUM-OXYGEN SYSTEM"
45 PRINT "    *******************************"
50 PRINT "               AUXILLIARIES               "
55 PRINT
60 PRINT "VARIABLE AUX. WT, #/AMP------------------";
65 INPUT WO
67 IF WO<0 THEN999
70 PRINT "FIXED AUX WT.  LBS----------------------";
75 INPUT W
80 PRINT
85 PRINT "               ACTIVATION                 "
90 PRINT
95 PRINT "ACTIVATOR CONSUPTION, #/FT.SQ.-----------";
100 INPUT W8
103 IF W8<0 THEN 50
105 PRINT "ACTIVATION STRUCTURE, #/CELL--------------";
110 INPUT W9
115 PRINT
120 PRINT "              CONVERTER                  "
125 PRINT
130 PRINT "ELECTRODES  FRAMES, #/FT.SQ----------";
135 INPUT W6
137 IF W6=0 THEN 85
140 PRINT "CONVERTER HARDWARE, #/FT.SQ/STACK-------";
145 INPUT W7
150 PRINT "CONVERTER LIFE, ACTIVATIONS(PLATES/H'DWR) ";
155 INPUT L6,L7
160 PRINT
165 PRINT "               CELL            "
170 PRINT
175 PRINT "O.C.VOLTS, VOLTS/CELL-------------------";
180 INPUT V(0)
185 IF V(0)=0 THEN 120
190 PRINT "CELL POLARIZATION DATA   "
195 PRINT "DATA PT     I,ASF  V,VOLTS"
200 PRINT "-------     -----  -------"
205 FOR F=1 TO 2
210 PRINTF;
215 INPUT J(F),V(F)
220 NEXT F
225 PRINT "THEO ANODE CONSUMPTION, #/AHR-----------";
230 INPUT W2
235 PRINT "THEO CATHODE CONSUPT'N, #/AHR-----------";
240 INPUT W1
245 PRINT "THEO ELECTROLYTE CONSUM., #/AHR-------";
250 INPUT W3
255 PRINT "EXCESS ELECTROLYTE,NO.  STOICS----------";
260 INPUT N1
265 PRINT "EXCESS ELECTROLYTE RECOVERED/ACTIVATION,0/0--";
270 INPUT R
275 PRINT "WEIGHT OF REACTANT STOREAGE,#/AHR AT 1AHR-";
280 INPUT W5
300 LET C=(J(2)/(V(0)-V(2))-J(1)/(V(0)-V(1)))/(V(1)-V(2))
305 LET B=J(1)/(V(1)-V(0))-C*(V(1)+V(0))
310 LET A=-B*V(0)-C*V(0)↑2
315 PRINT
320 PRINT "               MISSION                   "
325 PRINT
330 PRINT "NO.OF POWER LEVELS----";
334 INPUT N2
335 PRINT "LEVEL  WATTS"
340 FOR K=1 TO N2
345 PRINT K;
350 INPUT P(K)
355 NEXT K
360 PRINT "NO. OF CAPACITY LEVELS----";
365 INPUT N3
370 PRINT "LEVEL   WATTHOURS"
375 FOR L=1 TO N3
380 PRINT L;
385 INPUT Q(L)
390 NEXT L
400 FOR K=1 TO N2
402 PRINT
403 PRINT
405 FOR L=1 TO N3
407 PRINT
408 PRINT
410 PRINT "POWER LEVEL, WATTS-------------",P(K)
415 PRINT "CAPACITY, WATTHOURS------------",Q(L)
420 PRINT
425 PRINT "RATE,HRS","V/CELL","I,ASF","WT.LBS","WH/LB"
430 FOR N=5 TO 10
```

Table 25 (Cont'd)

METAL/OXYGEN CELL SYSTEM PROGRAM

```
433 LET X=0
435 LET T=Q(L)/(N*P(K))
440 LET E1=.319-.039*LOG (T)
445 LET V=V(0)-.01
450 LET J=A+B*V+C*V↑2
455 IF J<35 THEN 460
456 LET E2=J/(2.49*J-44)
457 GO TO 465
460 LET E2=J/(1.334+1.178*J)
465 LET E3=.74/(1.48/E2-.74)
470 LET S1=Q(L)/V*(W1+W2/(E2*(1-E1))+W3/E3*(1+N1*(1-R/100*(1-1/N))))
475 LET S2=W5*(Q(L)/V)↑.667
480 LET S3=P(K)/(V*J)*(W6*INT((N-.1)/L6+1)+W7*V/28*INT((N-.1)/L7+1))
485 LET S4=N*P(K)*W8/(V*J)+W9*(S1+S2+S3)
490 LET S5=P(K)*W0/V+W
495 LET S6=S1+S2+S3+S4+S5
500 IF X=0 THEN510
505 IF S6<S THEN 510
507 GO TO 525
510 LET S=S6
515 LET V1=V
520 LET J1=J
525 IF V<=V(0)/2 THEN 550
530 LET X=X+1
535 LET V=V-.01
540 GO TO 450
550 PRINT T,V1,J1,S,Q(L)/S
560 NEXT N
570 NEXT L
575 NEXT K
580 GO TO 160
999 END
```

```
MRPS3       9:34   JULY 16,1968

         ALUMINUM-OXYGEN SYSTEM
    *********************************
             AUXILLIARIES

VARIABLE AUX. WT, #/AMP-------------------?0
FIXED AUX WT.  LBS------------------------?5

             ACTIVATION

ACTIVATOR CONSUPTION, #/FT.SQ.------------?8E-4
ACTIVATION STRUCTURE, #/CELL---------------?0

            CONVERTER

ELECTRODES  FRAMES, #/FT.SQ-----------? .2
CONVERTER HARDWARE, #/FT.SQ/STACK-------?10
CONVERTER LIFE, ACTIVATIONS[PLATES/H'DWR] ? 1,10

             CELL

O.C.VOLTS, VOLTS/CELL--------------------?1.4
CELL POLARIZATION DATA
DATA PT    I,ASF  V,VOLTS
-------    -----  -------
 1     ?    50,    1.08
 2     ?   100,     .83
THEO ANODE CONSUMPTION, #/AHR-----------? 7.75E-4
THEO ELECTROLYTE CONSUM., #/AHR-------? 7.4E-4
EXCESS ELECTROLYTE,NO.  STOICS----------?1
EXCESS ELECTROLYTE RECOVERED/ACTIVATION,0/0--? 0

            MISSION

NO.OF POWER LEVELS----? 3
LEVEL  WATTS
 1     ?  100
 2     ?  200
 3     ?  500
NO. OF CAPACITY LEVELS----? 6
LEVEL   WATTHOURS
 1     ? 1E+3
 2     ? 1E+4
 3     ? 5E+4
 4     ? 1E+5
 5     ? 2E+5
 6     ? 5E+5
THEO CATHODE CONSUMP N, #/AHR---------? 2.06E-3
REACTANT STORAGE VESSEL, #/AHR AT 1AHR-? 4.015E-2
```

The specific heat generation (thermal energy per ampere-hour) within any cell system results from the difference between the overall enthalpy change for the system and the net electrical energy produced by the system. Thus, the specific heat generation in BTU per ampere-hour is:

$$q \text{ (BTU per ampere-hour)} = \frac{3.968 \times \Delta H}{26.8 \times n x \eta} - 3.414 \times V \quad (10)$$

3.968 = conversion factor kilocalories to BTU

26.8 = ampere-hours per gram equivalent

3.414 = conversion watthours to BTU

ΔH = enthalpy change of the system, KCal/g-mole

n = number of electrons involved in the electrochemical reaction

η = coulombic efficiency

V = operating cell voltage for minimum system weight

Note that V numerically represents watthours per ampere-hour as well as cell voltage.

Table 26

ENERGY DENSITY COMPARISON(1
ALUMINUM OXYGEN CELLS

Capacity Kilowatt Hours	Energy Density Watthours per pound											
	100 Watts				200 Watts				500 Watts			
	A(2	B(3	C(4	D(5	A	B	C	D	A	B	C	D
1	55	39	55	67	45	34.	45	53	33	25	33	37
10	138	100	152	196	128	95	140	178	107	84	116	143
50	182	152	214	260	176	148	206	250	164	139	190	227
100	195	175	235	278	191	171	229	270	182	163	216	253
200	206	195	253	291	202	192	248	285	195	186	239	273
500	216	220	272	303	214	218	268	300	209	214	263	292

1) Tabulated energy densities are results averaged over 5 to 10 activations. Maximum variation from average for any value was less than 8 percent. In the computation, no weight penalty for heat transfer has been allowed.

2) Oxygen source is chlorate candle

3) Oxygen source is compressed gas in steel cylinder

4) Oxygen source is compressed gas in filament wound sphere

5) Oxygen source is hydrogen peroxide

Table 27

HEAT TRANSFER MECHANISMS SUMMARY

ΔT (1	Environment (2	Heat Transfer Mechanism	Additional Weight Requirement
Negative	Gravity and ambient fluid	Natural convection	None or fins
Negative	No gravity plus ambient fluid	Forced convection	Pump or blower, fins
Negative	No gravity plus no ambient fluid	Radiation	Radiatior
Zero or positive	Any	Transpiration	Vaporizing fluid and storage container

1) T ambient - T cell, maximum

2) Surrounding cell during operation

For the aluminum/H_2O_2 cell system, ΔH is the enthalpy change for the reaction:

$$Al_{(s)} + \frac{3}{2}\eta H_2O_{2(a)} + 3(2-1.5\eta)H_2O_{(e)} \xrightarrow{3\eta e^-} 1.5(1-\eta)H_{2(g)} + Al(OH)_{3(s)} + 1.5(2-\eta)H_2O_{(g)} \qquad (11)$$

where it is assumed that the excess water required by the cell can be exhausted to space vacuum to provide some transpiration cooling. Under these conditions, the value of ΔH is:

$$\Delta H = 1.5(2-\eta)(-57.8) - 304.8 - 3(2-1.5\eta)(-68.32) - 1.5\eta(-45.8) \text{ K Cal/ g-mole}$$

$$\therefore \Delta H = (67.8 + 153\eta) \text{ K Cal / g-mole} \qquad (12)$$

When this result is combined with Equation 10, the final expression for the specific heat generation is:

$$q = \frac{0.0495}{\eta}(67.8 + 153\eta) - 3.414V = 7.58 + 3.36/\eta - 3.414V \qquad (13)$$

The results computed in the course of the previous optimization analysis indicate that the optimum operating cell voltage is about 1.2 volts per cell corresponding to a coulombic efficiency of about 75%. When these two values are employed in Equation 13, the estimated heat generation rate per watthour of electrical output is approximately

$$\frac{7.58 + 3.36/0.75 - 3.414(1.2)}{1.2} = 6.65 \frac{\text{B.T.U}}{\text{watt hour}} \qquad (14)$$

If no additional means for removing heat from the system is available (adiabatic system), the temperature rise during cell operation may be estimated from the equation:

$$(q/V) \times (Q/N) + (S/N) \times C_p \times \Delta T \qquad (15)$$

where:

q/V = BTU generated per watthour of electrical output

Q/N = watthours per discharge

S/N = pounds of batter per discharge

C_p = heat capacity = BTU per pound x °F

ΔT = temperature difference, °F

N = number of activations

Solving for the temperature rise, ΔT, and assuming an effective system heat capacity of 0.5 BTU per pound °F, Equation 15 reduces to:

$$\Delta T = \frac{q/V}{C_p}\left(\frac{Q}{S}\right) = \frac{6.65}{0.50}\left(\frac{Q}{S}\right) = 13.3 \times \frac{Q}{S} \qquad (16)$$

where:

Q/S = energy density of system in watthours per pound

Substitution of any of the energy densities of Table 26 into Equation 16 shows quite clearly that the generated heat must be removed from the metal/oxygen system, since the effective operating temperature range for the cells is only about 90°F (40 to 130°F).

Radiant Heat Transfer. The minimum surface area required for radiating the heat generated according to Equation 14 may be estimated from the following relationship:

$$\varphi = (q/V) \times P = \sigma \varepsilon A_{min} (T_1{}^4 - T_2{}^4) \qquad (17)$$

where:

φ = heat radiated, BTU per hour

q/V = BTU generated per watthour of output

P = power level in watts

σ = conversion factor with value 0.1713

ε = emmissivity of radiator surface

A_{min} = minimum radiator area in square foot

T_1 = maximum temperature of system, °K

T_2 = minimum temperature of system, °K

Assuming a maximum system temperature of 100°F, a minimum ambient temperature of 0°F, and an emissivity of 0.9, the minimum surface area, A_{min}, required for isothermal operation of a 100-watt system is

$$A_{min} = \frac{(q/V)_t \cdot \rho}{\sigma\epsilon(560^4 - 460^4)} = \frac{(6.65)\ (100)}{0.9(0.1713)(5.6^4 - 4.6^4)} = 7.2 \text{ square feet} \qquad (18)$$

If the cell system is assumed to be in a spherical configuration with an effective density of about 50 pounds per cubic foot, the exposed surface area of the system can be expressed as a function of system weight, viz.,

$$Vol_{sphere} = \frac{4}{3}\pi R^3 \qquad (19)$$

$$A_{sphere} = 4\pi R^2 = 4\pi\left(\frac{3V_{sphere}}{4\pi}\right)^{2/3} = (4\pi)^{1/3}(3M/C)^{2/3} = \left(\frac{36\pi}{2500}\right)^{1/3}(5)^{2/3} \qquad (20)$$

$$\therefore A_{min} = 0.356\ (S)^{2/3} = 7.2 \text{ square feet}$$

where:

ρ = system density, 50 pounds per cubic foot

S = system weight, pounds (without radiator)

Solving Equation 20 for the minimum system weight (S_{min})

$$S_{min} = \left(\frac{7.2}{0.356}\right)^{3/2} = 95 \text{ lbs/activation} \qquad (21)$$

An analysis of the results in Table 26 shows that only the very largest systems (> 200 kilowatt-hours capacity) have inherent surface areas which are large enough to provide the radiant heat transfer rates required under the most favorable conditions. In smaller systems, or under less favorable conditions, the additional weight associated with extended radiational surfaces for each activation, severely limits the overall system energy density. For example, Table 26 shows the energy density of a 1-kilowatt hour Al/H_2O_2 system to be about 67 watthour per pound. Under the above assumed conditions, the energy density of this system, after adding a 7.2 square foot radiator for each activation is given by the expression:

$$\left(\frac{\text{watthours}}{\text{pound}}\right)_s = \frac{1000}{\frac{1000}{67} + 7.2\ NP^1} = \frac{1000}{15 + 7.2\ N\rho^1} \qquad (22)$$

where:

$\left(\frac{\text{watthours}}{\text{pound}}\right)_s$ = new energy density with radiator

N = number of activations/mission

ρ^{1} = density of radiator, pounds per square foot

Assuming a radiator density of 1 pound per square foot, the energy density of this system for 5 activations is reduced to:

$$\left(\frac{\text{watthours}}{\text{pound}}\right)_s = \frac{1000}{15 + 36} = \frac{1000}{51} = 19.6 \qquad (23)$$

Heat Transfer by Transpiration. The quantity of water required for transpirational cooling of the cell system is related to the specific heat generation and the total ampere-hours of discharge required by the mission:

$$M_{H_2O} = \frac{(q/V)}{\Delta h} = \frac{Q}{V}\,(g/\Delta h) \qquad (24)$$

where:

M_{H_2O} = pounds of water required

q/V = BTU generated per watthour of electrical output

Q = watthours per mission

Δh = enthalpy of water evaporation, K Cal per mole

Thus, the transpirational cooling weight debit is a function of the operating cell voltage. As a result, the optimum system weight with transpirational cooling will occur at a different voltage than that obtained in the original analysis, thereby producing the results in Table 26.

The expression for total system weight with transpirational cooling is

$$S = S_A + S_B + S_C \qquad (25)$$

where:

$$S_A = \frac{Q}{V}\left(W_1 + \frac{Q}{V}^{-1/3} W_2 + W_9\right)$$

$$S_B = \frac{NP}{VJ}\left(W_3 + \left(\frac{P}{VJ}\right)^{-1/3} W_4 + \frac{V}{E} \cdot W_5\right)$$

$$S_C = \frac{P}{V} W_6 + W_7$$

This is as before, except that W_9 has been added; W_9 represents the weight of water required for transpirational cooling of the cell. Table 2 gives the meaning of the other terms.

$$W_9 = q/\Delta h \qquad (26)$$

where:

q = BTU generater per ampere-hour

The converter weight, $\mathcal{S}_B$, must include an allowance for the storage of water; this is done by adding an appropriate factor to W_4.

A comparison of the values of each term in Equation 25 (expanded) shows that the transpiration cooling water requirement, $q/\Delta h$, is the largest weight factor in the metal-peroxide system. Since the catalytic decomposition of the peroxide itself accounts for a substantial portion (1.66 BTU's per ampere-hour out of about 8 BTU's per ampere-hour total) of the total heat generated in the system, compressed oxygen-gas storage must be reconsidered.

The derived equation for this system must include provision for gas storage weight and water storage weight. This is done by modifying the value of W_4. It must also take into account the difference in heat generated per ampere-hour of electrical output.

In addition to the heat of peroxide decomposition, the total heat generation is influenced by the heat of formation of the metal hydroxide reaction product. In view of the significant difference between the heats of formation of zinc hydroxide and aluminum hydroxide (11.4 BTU's per ampere-hour versus 15.1 BTU's per ampere-hour respectively), the zinc/oxygen system must also be reconsidered to determine the best anode choice (maximum system energy density) under conditions where transpirational cooling is necessary.

Equation 25 (expanded) was employed as the basis of four similar computer programs (Table 28 through 31, corresponding to the aluminum/hydrogen peroxide, aluminum/high-pressure oxygen, zinc/hydrogen peroxide, and zinc/high-pressure oxygen candidate systems respectively) to compute the optimum system. The corresponding system energy density for each set of mission parameters is summarized in Tables 32 and 33. Table 34 gives the calculated energy density results for the systems as a function of mission capacity, power level, and number of activations. The two values in each entry of Table 34 correspond to 10 and 5 activations respectively.

These results show that the zinc/oxygen system offers better energy densities than the aluminum/oxygen system over the entire spectrum of mission possibilities when transpirational cooling (evaporation of water from the system) is required for temperature moderation. It can also be seen that high-pressure gaseous oxygen storage results in higher system energy densities than liquid peroxide in the larger systems (> 50 kilowatt hours) where the storage vessel weight is small relative to the overall system weight. In the smaller systems, hydrogen peroxide appears to be a more efficient means for storing reactant oxygen in spite of the additional cooling requirement associated with its decomposition.

The results are straight forward, and no special comment on them is offered.

Table 28

ALUMINUM/HYDROGEN PEROXIDE SYSTEM PROGRAM (MRAP)

```
MRAP      10:01   AUG.8,1968

10 READ V(0)
15 FOR F=1 TO2
20 READ J(F),V(F)
25 NEXT F
30 LET C=(J(2)/(V(0)-V(2))-J(1)/(V(0)-V(1)))/(V(1)-V(2))
35 LET B=J(1)/(V(1)-V(0))-C*(V(1)+V(0))
40 LET A=-B*V(0)-C*V(0)↑2
50 FOR K=1 TO3
60 READ P(K)
65 NEXT K
70 FOR L=1 TO 6
80 READ Q(L)
85 NEXT L
90 PRINT"**************ALUMINUM/PEROXIDE SYSTEM**************"
100 FOR K=1 TO3
110 PRINT "       POWER LEVEL,WATTS-----",P(K)
120 PRINT
125 PRINT"KWHRS","V/CELL","I,ASF","WT.LBS","WH/LB."
130 FOR L=1 TO6
140 FOR N=5 TO10
150 LET X=0
160 LET T=Q(L)/(N*P(K))
170 LET E1=.319-.039*LOG(T)
180 LET V=V(0)-.01
190 LET J=A+B*V+C*V↑2
200 IF J<35 THEN 230
210 LET E2=J/(2.49*J-44)
220 GO TO 240
230 LET E2=J/(1.334+1.178*J)
240 LET S1=.001*Q(L)/V*(6.8+6.32/E2-3.42*V+.775*(1+E1)/E2)
250 LET S2=(7.8E-3)*N*(Q(L)/(N*V)*(6.8+6.32/E2-3.42*V))↑.667
260 LET S3=P(K)/(V*J)*(N*.2008+10*V/28)
270 LET S=S1+S2+S3+5
280 IF X=0 THEN 310
290 IF S<W THEN 310
300 GO TO 340
310 LET W=S
320 LET V1=V
330 LET J1=J
340 IF V<=V(0)/2 THEN 380
350 LET X=X+1
360 LET V=V-.01
370 GO TO 190
380 PRINT Q(L)/1000,V1,J1,W,Q(L)/W
390 NEXT N
400 PRINT
410 NEXT L
420 PRINT
430 NEXT K
440 DATA 1.4
450 DATA 50,1.08
460 DATA 100,.83
470 DATA 100,200,500
480 DATA 1E+3,1E+4,5E+4,1E+5,2E+5,5E+5
500 END
```

Table 29

ALUMINUM/HIGH-PRESSURE OXYGEN SYSTEM PROGRAM (MRAO)

```
MRAO       14:02    AUGUST 12,1968

10 READ V(0)
15 FOR F=1 TO2
20 READ J(F),V(F)
25 NEXT F
30 LET C=(J(2)/(V(0)-V(2))-J(1)/(V(0)-V(1)))/(V(1)-V(2))
35 LET B=J(1)/(V(1)-V(0))-C*(V(1)+V(0))
40 LET A=-B*V(0)-C*V(0)↑2
50 FOR K=1 TO3
60 READ P(K)
65 NEXT K
70 FOR L=1 TO 6
80 READ Q(L)
85 NEXT L
90 PRINT"**************ALUMINUM/PEROXIDE SYSTEM**************"(SIC)
100 FOR K=1 TO3
110 PRINT "        POWER LEVEL,WATTS-----",P(K)
120 PRINT
125 PRINT"KWHRS","V/CELL","I,ASF","WT.LBS","WH/LB."
130 FOR L=1 TO6
140 FOR N=5 TO10
150 LET X=0
160 LET T=Q(L)/(N*P(K))
170 LET E1=.319-.039*LOG(T)
180 LET V=V(0)-.01
190 LET J=A+B*V+C*V↑2
200 IF J<35 THEN 230
210 LET E2=J/(2.49*J-44)
220 GO TO 240
230 LET E2=J/(1.334+1.178*J)
240 LET S1=.001*Q(L)/V*(4.95+6.51/E2-3.42*V+.775*(1+E1)/E2)
250 LET S2=N*((Q(L)/(N*V))↑.667)
251 LET S2=S2*(3.78E-2+(7.8E-3)*(4.29+6.51/E2-3.42*V)↑.667)
260 LET S3=P(K)/(V*J)*(N*.2008+10*V/28)
270 LET S=S1+S2+S3+5
280 IF X=0 THEN 310
290 IF S<W THEN 310
300 GO TO 340
310 LET W=S
320 LET V1=V
330 LET J1=J
340 IF V<=V(0)/2 THEN 380
350 LET X=X+1
360 LET V=V-.01
370 GO TO 190
380 PRINT Q(L)/1000,V1,J1,W,Q(L)/W
390 NEXT N
400 PRINT
410 NEXT L
420 PRINT
430 NEXT K
440 DATA 1.4
450 DATA 50,1.08
460 DATA 100,.83
470 DATA 100,200,500
480 DATA 1E+3,1E+4,5E+4,1E+5,2E+5,5E+5
500 END
```

Table 30

ZINC/HYDROGEN PEROXIDE SYSTEM PROGRAM (MRZP)

```
MRZP      10:04    AUG.8,1968

10 READ V(0)
15 FOR F=1 TO2
20 READ J(F),V(F)
25 NEXT F
30 LET C=(J(2)/(V(0)-V(2))-J(1)/(V(0)-V(1)))/(V(1)-V(2))
35 LET B=J(1)/(V(1)-V(0))-C*(V(1)+V(0))
40 LET A=-B*V(0)-C*V(0)↑2
50 FOR K=1 TO3
60 READ P(K)
65 NEXT K
70 FOR L=1 TO 6
80 READ Q(L)
85 NEXT L
90 PRINT"**********ZINC/PEROXIDE SYSTEM*****************"
100 FOR K=1 TO3
110 PRINT "        POWER LEVEL,WATTS-----",P(K)
120 PRINT
125 PRINT"KWHRS","V/CELL","I,ASF","WT.LBS","WH/LB."
130 FOR L=1 TO6
140 FOR N=5 TO10
150 LET X=0
160 LET T=Q(L)/(N*P(K))
170 LET E1=.24-.029*LOG(T)
180 LET V=V(0)-.01
190 LET J=A+B*V+C*V↑2
240 LET S1=.001*Q(L)/V*(9.04-3.42/V+3.69*(1+E1))
250 LET S2=((7.8E-3)*N*(Q(L)/(N*V))↑.667)*(2.11+(5.97-3.42*V)↑.667)
260 LET S3=P(K)/(V*J)*(N*.2024+10*V/28)
270 LET S=S1+S2+S3+5
280 IF X=0 THEN 310
290 IF S<W THEN 310
300 GO TO 340
310 LET W=S
320 LET V1=V
330 LET J1=J
340 IF V<=V(0)/2 THEN 380
350 LET X=X+1
360 LET V=V-.01
370 GO TO 190
380 PRINT Q(L)/1000,V1,J1,W,Q(L)/W
390 NEXT N
400 PRINT
410 NEXT L
420 PRINT
430 NEXT K
440 DATA 1.35
450 DATA 50,1.2
460 DATA 100,1.11
470 DATA 100,200,500
480 DATA 1E+3,1E+4,5E+4,1E+5,2E+5,5E+5
500 END
```

Table 31

ZINC/HIGH-PRESSURE OXYGEN SYSTEM PROGRAM (MRZO)

```
MRZO        12:09    AUGUST 12,1968

9
10 READ V(0)
15 FOR F=1 TO2
20 READ J(F),V(F)
25 NEXT F
30 LET C=(J(2)/(V(0)-V(2))-J(1)/(V(0)-V(1)))/(V(1)-V(2))
35 LET B=J(1)/(V(1)-V(0))-C*(V(1)+V(0))
40 LET A=-B*V(0)-C*V(0)↑2
50 FOR K=1 TO3
60 READ P(K)
65 NEXT K
70 FOR L=1 TO 6
80 READ Q(L)
85 NEXT L
90 PRINT"***********ZINC/HP O2 SYSTEM***********************"
100 FOR K=1 TO3
110 PRINT "        POWER LEVEL,WATTS-----",P(K)
120 PRINT
125 PRINT"KWHRS","V/CELL","I,ASF","WT.LBS","WH/LB."
130 FOR L=1 TO6
140 FOR N=5 TO10
150 LET X=0
160 LET T=Q(L)/(N*P(K))
170 LET E1=.24-.029*LOG(T)
180 LET V=V(0)-.01
190 LET J=A+B*V+C*V↑2
240 LET S1=.001*Q(L)/V*(7.3-3.42*V+3.69*(1+E1))
250 LET S2=((Q(L)/(N*V))↑.667)*N*(3.78E-2+(7.8E-3)*(6.64-3.42*V)↑.667)
260 LET S3=P(K)/(V*J)*(N*.2024+10*V/28)
270 LET S=S1+S2+S3+5
280 IF X=0 THEN 310
290 IF S<W THEN 310
300 GO TO 340
310 LET W=S
320 LET V1=V
330 LET J1=J
340 IF V<=V(0)/2 THEN 380
350 LET X=X+1
360 LET V=V-.01
370 GO TO 190
380 PRINT Q(L)/1000,V1,J1,W,Q(L)/W
390 NEXT N
400 PRINT
410 NEXT L
420 PRINT
430 NEXT K
440 DATA 1.35
450 DATA 50,1.2
460 DATA 100,1.11
470 DATA 100,200,500
480 DATA 1E+3,1E+4,5E+4,1E+5,2E+5,5E+5
500 END
```

Table 32

METAL/OXYGEN CELL REACTIONS

System	Assumed Cell Reaction	ΔH, KCal/Mole
Al/H_2O_2	$Al_{(s)}+\frac{3}{2}\eta\, H_2O_{2(aq)} + 3(2-\frac{3}{2}\eta)\, H_2O_{(\ell)} \xrightarrow{3\eta e^-} 1.5(1-\eta)\, H_{2(g)} + Al(OH)_{3(s)} + (3-\frac{3}{2}\eta)H_2O_{(g)}$	$68 + 153\eta$
$Al/H.P.O_2$	$Al_{(s)}+\frac{3}{4}\eta\, O_{2(g)} + 3(2-\eta)\, H_2O_{(\ell)} \xrightarrow{3\eta e^-} 1.5(1-\eta)\, H_{2(g)} + Al(OH)_{3(s)} + (3-\frac{3}{2}\eta)H_2O_{(g)}$	$68 + 118\eta$
Zn/H_2O_2	$Zn_{(s)} + H_2O_{2(aq)} + 2(1-f)KOH_{(aq)} \xrightarrow{2e^-} f\,Zn(OH)_{2(s)} + (1-f)K_2ZnO_{2(aq)} + 2(1-f)H_2O_{(g)}$	84.7 (1
$Zn/H.P.O_2$	$Zn_{(s)}+\frac{1}{2}O_{2(g)} + H_2O_{(\ell)} + 2(1-f)KOH_{(aq)} \xrightarrow{2e^-} f\,Zn(OH)_{2(s)} + (1-f)K_2ZnO_{2(a\;)} + 2(1-f)H_2O_{(g)}$	61,2 (1

1) f assumed as constant (f = 0.9) - independent of reaction rate

Table 33

METAL/OXYGEN SYSTEM PARAMETERS FOR TRANSPIRATION-COOLED SYSTEMS

Parameter (Program)	Al/H_2O_2 (MRAP)	$Al/H.P.O_2$ (MRAO)	Zn/H_2O_2 (MRZP)	$Zn/H.P.O_2$ (MRZO)
1. Equivalent Weights				
W_1, pounds anode per ampere hour (2)	$7.75 \frac{1+\mu}{\eta} \cdot 10^{-4}$	$7.75 \frac{1+\mu}{\eta} \cdot 10^{-4}$	$3.69 \cdot 10^{-3}(1+\mu)$	$3.69 \cdot 10^{-3}(1+\mu)$
W_2, pounds oxident per ampere hour	$1.4 \cdot 10^{-3}$	$6.60 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$	$6.60 \cdot 10^{-4}$
W_3, pounds electrolyte per ampere hour	$(3.11/\eta - 2.31) \cdot 10^{-3}$	$(3.11/\eta - 1.55) \cdot 10^{-3}$	$1.38 \cdot 10^{-3}$	$2.12 \cdot 10^{-3}$
$q/\Delta h$ pounds cooling water per ampere hour (3)	$(7.6 + 3.36/\eta - 3.42V) \cdot 10^{-3}$	$(5.84 + 3.40/\eta - 3.42V) \cdot 10^{-3}$	$(6.26 - 3.42V) \cdot 10^{-3}$	$(4.52 - 3.42V) \cdot 10^{-3}$
K_o, (pounds horsepower O_2 sphere)/pound $O_2)^{2/3}$ (4)	- - -	5.06	- - -	5.06
K_e, $\frac{\text{(pounds liquid storage vessel)}}{\text{(pounds stored liquid)}^{2/3}}$	0.87	0.87	0.87	0.87
2. Converter Weights				
W_6, pounds cathode per square foot	0.2	0.2	0.2	0.2
W_g, pounds separator per square foot	$8.0 \cdot 10^{-4}$	$8.0 \cdot 10^{-4}$	$2.4 \cdot 10^{-3}$	$2.4 \cdot 10^{-3}$
W_7, pounds frame per square foot per stack	10.0	10.0	10.0	10.0
3. Auxiliary Weight				
W, pounds instruments and controls	5.0	5.0	5.0	5.0

1) Parameters refer to terms in computer program, not to Equation 25

2) Includes weight of alloy additives and current collector

3) Assumes Δh = 1000 BTU's per pound (of water)

4) Vessel size factor for filament wound, high-pressure sphere

Table 34

METAL-OXYGEN MULTIPLE RESERVE BATTERY SYSTEM ENERGY DENSITY, WATTHOUR PER POUND

Kilowatt Hours	O_2 Source(1	100 Watts		200 Watts		500 Watts	
		Aluminum	Zinc	Aluminum	Zinc	Aluminum	Zinc
1	P	35-41	46-51	29-36	41-47	20-26	35-41
	O_2	30-36	40-46	25-32	36-43	18-24	31-38
10	P	72-79	92-101	68-75	87-95	59-67	78-87
	O_2	65-74	87-98	61-70	82-93	54-63	74-85
50	P	90-95	118-125	88-93	113-121	83-89	106-114
	O_2	87-94	120-132	85-93	115-127	80-89	108-120
100	P	95-99	127-133	94-98	123-130	90-95	116-123
	O_2	95-101	133-144	96-100	129-140	90-97	122-133
200	P	99-102	134-140	98-102	131-137	96-100	125-132
	O_2	102-107	146-156	101-106	141-152	98-104	135-146
500	P	103-106	143-148	103-105	140-145	102-104	135-140
	O_2	109-113	160-169	108-113	156-166	107-112	151-160

1) P denotes H_2O_2 (liquid storage)

O_2 denotes high pressure O_2 (gas storage)

Section 5

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