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**FINAL REPORT TO UNITED STATES
ATOMIC ENERGY COMMISSION . . .**

**POWER FLATTENING STUDIES FOR
RADIOISOTOPE-THERMOELECTRIC
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GENERATORS.**

GENERAL INSTRUMENT CORP. -- THERMOELECTRIC DIVISION

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THE THERMOELECTRIC DIVISION
of the
THE GENERAL INSTRUMENT CORPORATION
FINAL REPORT
POWER FLATTENING STUDIES FOR
RADIOISOTOPE FUELED THERMOELECTRIC GENERATORS

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FOREWORD

This is the final report of work performed under A.E.C. contract AT(30-1) 2783. This report covers the period from April 1961 through February 1963. The work was sponsored by the Reactor Development Branch of the Atomic Energy Commission (New York Operations Office).

Power Flattening Studies for Radioisotope Fueled Thermoelectric Generators

ABSTRACT

The natural exponential decay of a radioisotope used as a heat source for a thermoelectric generator makes the use of a "power flattening" device highly desirable, especially when the duration of the mission is large compared to the half-life of the radioisotope. The power flattening devices considered in this report either dump excess heat outside the thermoelectric generator or use the characteristics of the generator to absorb the excess heat and thereby regulate the hot junction temperature.

A number of power flattening devices have been studied both analytically and experimentally with a view toward operability in space. The most promising concepts are (a) to utilize a secondary radiator of variable area; (b) to provide thermal shunts that are sequentially removed during the mission; (c) to use a secondary radiator coupled to the heat source through a slowly evaporating thermal connection.

1. SUMMARY

The natural exponential decay of a radioisotope used as a heat source for a thermoelectric generator makes the use of a power flattening device highly desirable. As used in this connection, a power flattening device is defined as a means of regulating or distributing the thermal output of a radioisotope heat source so as to reduce variations in the hot junction temperature of an associated thermoelectric generator to an acceptable level. As a consequence, the power flattening device tends to maintain constant heat flow through the active portion of the generator. This report is concerned mainly with space missions although some of the devices investigated can also be adapted for power flattening in non-space missions.

1.1 Work Performed

1. An analysis of the behavior of an unregulated radioisotope-thermoelectric generator (RTG) was performed in which the variation in hot junction temperature (T_h) for a typical lead telluride generator was explored as a function of the ratio of mission time to half-life (Θ_F/h). For example, for $\Theta_F/h = .75$ the variation in hot junction temperature was from 1200 F at start-of-life (Θ_0) to 800 F at end-of-life (Θ_F). A variation of this magnitude has serious deleterious effects of system efficiency and reliability.

2. Potential power flattening devices were divided into two classes for purposes of analysis and discussion.

Class I. All heat is rejected through a single radiator and heat flow is regulated by shunting heat around the active thermocouples by one means or another.

Class II. A secondary radiator is provided to reject all excess heat, this radiator being controlled so as to vary with time in area, emissivity or effectiveness in the desired manner.

3. Two Class I systems were studied. The least promising one uses a number of thermocouples in a short-circuited condition at Θ_0 to give maximum Peltier heat pumping. Analysis confirmed by experiment showed that one could expect a variation in T_h of 250 F for $\Theta_F/h = .75$. Analysis of another Class I system showed greater promise. This system provides extra bypass thermocouples at Θ_0 to shunt excess heat. The bypass couples are removed sequentially

from the thermal path between source and radiator by dumping a fluid heat transfer medium. At Θ_F an optimized generator remains.

4. Five Class II methods were studied, three of which are considered promising.
 - a) In the variable thermal contact resistance method, the thermal contact resistance between heat source and secondary radiator is increased by slowly reducing the gas pressure loading of two surfaces in contact. Analysis confirmed by experiment failed to show promise of fulfilling weight and reliability criteria.
 - b) In the variable thermal conductivity method advantage is taken of the change of thermal conductivity with temperature of various ceramic insulations. A material with a negative rate of change is placed between source and generator while a second material having a positive rate of change is placed between source and secondary radiator. A search failed to discover materials having sufficient variation in conductivity to provide good regulation of the system.
 - c) In the variable area method a secondary radiator using sequentially ejected segments provides control of the excess heat. Analysis confirmed by experiment showed that three ejection sequences provide satisfactory regulation for $\Theta_F/h = .75$.
 - d) In the variable emissivity method the secondary radiator is coated with a high emissivity material over a base coating of a very low emissivity material. The former material gradually evaporates in use exposing the low emissivity coating underneath in the desired time sequence. Analysis indicates that this is a promising technique for $\Theta_F/h \approx .75$.
 - e) Finally, the secondary radiator can be connected to the heat source by means of a material that slowly evaporates when heated in space vacuum. The gradual decrease in area reduces the excess heat being dumped. This evaporating conductance method shows promise for larger values of Θ_F/h .

1.2 Conclusions

Analysis of the behavior of a radioisotope-thermoelectric generator without power flattening showed that the essential function of a power flattening device is to control the heat flow through the thermoelectric generator so as to maintain constant hot junction temperature. As a corollary to this function the electrical power output of the generator is also held constant.

A number of power flattening devices were conceived, analyzed and evaluated in this program. The main criterion was to increase overall reliability for space missions by eliminating moving mechanical parts. Of the seven devices that were intensively studied, three appear to be most worthy of consideration and further development. These are:

1. The bypass generator method described in section 4.3 that provides bypass thermocouples at start-of-life to divert excess heat. The bypass couples are sequentially removed from the thermal and electrical circuits during the mission.
2. The variable radiator area method using a secondary radiator with sequentially ejected segments to control the amount of heat diverted around the generator. This method is analyzed in section 4.5 and test results reported in section 5.4.
3. The variable base area method described in section 4.7 controls heat flow to a secondary radiator by use of a connecting material that slowly evaporates when heated in space vacuum. A limited survey showed a wide variety of potentially useful connecting materials.

All three of the above methods have several advantages in common:

- a) Fail-safety in that failure of the power flattening system is most likely to be in the direction of lower rather than higher hot junction temperature.
- b) High system "effectiveness" because heat diversion at end-of-life can be reduced to a very low value.
- c) No moving mechanical parts (if we do not include the ejection mechanism in the variable radiator area

method which can be unlatched by explosive bolts or fusible links and ejected by simple springs).

Among the three chosen methods the variable base area method using an evaporating conductance is the only one that does not entail provision of auxiliary timing controls. This method has the advantages of simplicity in physical construction, high effectiveness for large values of θ_F/h and potentially very lightweight since high radiator temperatures can be employed. The main problem in connection with this method (or with the related variable emissivity method described in section 4.6) is to develop and test suitable evaporating materials in a simulated space environment. The analysis of this device presented in section 4.7 is relatively straight-forward but requires the use of various assumptions connecting equilibrium and non-equilibrium theory.

Comparison of the bypass generator method and the variable radiator method shows that the main difference is in the degree of sophistication of the control techniques. In one case the controls act on internal generator parts and in the other on external radiator segments. A more detailed analysis, design, and testing program is required to resolve the choice between these two methods. However, these methods appear to have one advantage over the variable base area method. This is that the control sequence can be directly related to and affected by the actual generator temperatures if desired, while in the variable base area system the rate of evaporation is directly related to fuel source temperature and cannot be controlled by the generator temperature. Another advantage is that the bypass generator and variable radiator area methods can be completely tested and proven without the need for simulation of space environment.

2. INTRODUCTION

As a result of the successful demonstration of RTG systems for space auxiliary power service, and in view of the urgent needs for higher power systems of high reliability, it has become important to review the important characteristics of RTG systems in greater detail than has been heretofore possible. One of the most important factors in the efficient utilization of certain high energy density radioisotopes is the power flattening mechanism. The exponential decay of radioisotope fuels makes the use of a power flattening device highly desirable, especially when the duration of the mission is largely compared to the half-life of the radioisotope. In an unregulated RTG there may be serious deleterious effects on efficiency and reliability due to the uncontrolled variation in thermocouple junction temperatures. Previously known solutions of the power flattening problem are described in references 3 and 4.

2.1 Purpose and Scope

The purposes of this program have been (a) to analyze the behavior of RTG systems as affected by variable heat flux; (b) to originate new ideas for power flattening methods; (c) to analytically and experimentally evaluate promising methods of power flattening.

The scope of the program has been limited, particularly in experimental aspects. This report is therefore to be considered in the nature of a preliminary survey.

2.2 Technical Background

2.2.1 Radioisotope Decay Characteristics

The variation in radioisotope heat output due to exponential decay in the number of radioactive nuclei present is given by

$$* \quad Q_I(\theta) = Q_{I_0} e^{-\lambda \theta} \quad 2.2.1$$

since the heat output is proportional to the number of nuclei present. The decay constant λ is also given by $\lambda = h/.693$ so that

$$Q_I(\theta) = Q_{I_0} e^{-.693\theta/h} \quad 2.2.2$$

* All symbols are defined in the table in Appendix 6.1. In some instances the definitions are repeated in the body of the text. Brackets [] will be used to denote references listed in Appendix 6.2

In 2.2.1, Q_{I_0} represents the heat output of the source at any suitable reference zero time (θ_0). We will also use the symbol θ_F to represent the duration of a mission; thus the ratio of heat output at end-of-life to start-of-life is

$$Q_{IF}/Q_{I_0} = e^{-.693\theta_F/h} \quad \dots 2.2.3$$

Figure 2.2.1 shows the value of the heat ratio vs. θ/h and Figure 2.2.2 shows this ratio plotted against θ_F for three potentially useful radioisotope fuels - cerium-144, curium-242 and polonium-210.

The subject of radioisotope selection for RTG applications has been well-covered elsewhere [2,3] and will not be reviewed here except to note that the three radioisotopes mentioned above appear to be among the most useful presently available from the standpoints of high energy density, cost and availability. (The two other leading candidates for fuels are Strontium-90 ($h = 27.7$ years) and Plutonium-238 ($h = 89.6$ years). Neither of these requires power flattening for missions presently contemplated but use of either of these radioisotopes presents other knotty problems of safety and availability).

2.2.2 Heat Radiation in Space

In space applications the only mode of heat rejection available for thermoelectric generators or any other thermodynamic "engine" is by radiation to space. The governing equation is

$$Q_R = \epsilon \eta \sigma A (T_R^4 - T_S^4) \quad \dots 2.2.4$$

where

- ϵ = total hemispherical emissivity
- η = radiator efficiency
- σ = Boltzmann's constant
= $.1713 \times 10^{-8}$ Btu/hr ft²(°R)⁴
- A = radiator area, ft.²
- T_R = radiator base temperature, °R
- T_S = sink temperature, °R

FIG. 2.21 H. J. R. no. 1's mission Tu 1.1 - H. J. R. no. 1's mission

In this report we will be able to neglect the T_s^4 term in comparison to T_R^4 . The effective sink temperature in the solar system is approximately 460R. With $T_R = 860$, T_s^4 equals only 8% of T_R^4 . We will also neglect the small secondary effects of absorbed radiation from the earth and the sun. The net heat rejection from the radiator is therefore given by

$$Q_R = \epsilon \eta \sigma A T_R^4 \quad \dots 2.2.5$$

The emissivity of any real material is a complicated function of the wavelength of the radiation being considered (λ) and the surface temperature (T). In following sections the following defining equation for ϵ will be necessary:

$$\epsilon = \frac{\int_0^\infty \epsilon(\lambda, T) p(\lambda, T) d\lambda}{\int_0^\infty p(\lambda, T) d\lambda} \quad \dots 2.2.6$$

where

$\epsilon(\lambda, T)$ = spectral hemispherical emissivity at wavelength λ and temperature T

$p(\lambda, T)$ = radiation density of a black body at λ and T.

In addition, for preliminary analysis it is sufficiently accurate to take hemispherical and normal emissivities to be equal. Actually, this is approximately true except for highly polished metals which would not be used for heat radiators.

2.2.3 Thermoelectric Generator Characteristics

A brief review of the characteristics of thermoelectric generators is needed to establish criteria for evaluating power flattening devices. The efficiency of a thermoelectric generator (TEG), not including effects of contact resistance or extraneous heat losses and assuming that thermoelectric properties are temperature invariant, is given by [1] ,

$$\eta_{TE} = \frac{(T_h - T_c)}{T_h} \frac{\frac{m}{m+1}}{1 + \frac{KR_G}{\alpha^2} \frac{m+1}{m} - \frac{1}{2}(T_h - T_c) \frac{1}{m+1}} \dots 2.2.7$$

The efficiency depends only on (a) junction temperatures, T_h , T_c ; (b) selected value of the resistance ratio $m=R_L/R_G$; and (c) properties of the thermoelectric material given by the figure of merit $Z = KR_G/\alpha^2$. The figure of merit Z is also a function of temperature so that the efficiency depends strongly on the temperature levels of the generator. In general, T_h is chosen as high as possible consistent with thermoelectric material and fuel container integrity. The lower limiting value of T_c is governed by radiator weight limitations. Since radiant heat transfer varies as T_c^4 it is clear that space TEG systems will tend to optimize at fairly high values of T_c . Thus it is necessary in the interest of weight conservation to operate at as high a level of T_h as possible.

A number of practical factors limit the value of T_h . Extraneous heat losses, i.e., heat from the source that does not pass through the thermocouples, tend to increase unless added insulation is provided. Degradation in thermoelectric materials as a result of material sublimation and/or thermal stresses is a strong function of temperature. In discussing the power flattening problem, the specific limiting temperature is not particularly germane. The important point is that all known thermoelectric materials have certain limits. Therefore, the main purpose of the power flattening device is to ensure that the safe temperature limit is not exceeded and at the same time permit the operation of the RTG at the highest safe level throughout the useful life of the system. Without the power flattening device, the system would have to be constrained to operate at lower than maximum efficiency throughout the mission, reaching maximum only at the very end-of-life. This would entail a larger radioisotope inventory than necessary and a greater radiator surface to dissipate the corresponding larger heat flow through the system.

Section 3.4 gives a detailed analysis of the behavior of an unregulated RTG. The use of a voltage or cur-

rent regulator does not affect the thermal behavior of the system except as it affects the stabilization of temperatures in the case of varying electrical loads. This point is clearly shown in the analysis given in Section 3.4

2.3 Environmental Factors and Criteria for Comparison

The power flattening device must operate reliably under the environmental conditions imposed in space; i.e. high vacuum, zero or low gravity, meteoroid bombardment, ultra-violet and cosmic irradiation, etc. Vehicle launch conditions must also be considered. Highest reliability under these circumstances must be attributed to power flattening systems offering the following features: no moving parts; no fluid-containing parts vulnerable to meteoroid puncture; no organic or other materials subject to radiation damage; no force reaction on the vehicle; minimum disturbance in the thermal and momentum balance of the vehicle. Of course, the power flattening device must tend to fail-safe; i.e., failures must be such as to lead to lower rather than higher thermoelectric temperatures at the cost of lower efficiency.

In this connection, power flattening systems designed until now have been of two types: (a) one form or another of mechanical shutter as illustrated in Figure 2.3.1, or (b) utilizing a heat conducting fluid such as helium gas that is gradually leaked out into space during the course of the mission. Both of these types fail to fulfill one or more of the above-mentioned criteria. Hence, the requirement has arisen for investigation and evaluation of other power flattening devices.

In addition to the criteria already noted, the usual requirements of space hardware also apply: light weight, minimum envelope, adaptability to a range of power levels, ease of integration into vehicle envelope.

FIGURE 2.3.1

POWER FLATTENING BY A MECHANICALLY OPERATED SHUTTER.

3. SYSTEMS ANALYSIS

3.1 Behavior of a Radioisotope-Thermoelectric Generator System Without Power Flattening

The analysis that follows is concerned chiefly with the variation in hot junction temperature caused by the exponential variation in heat flux through a thermoelectric generator when there is no power flattening device associated with the system. It will become apparent that the use of a voltage or current regulator does not affect the analysis.

The analytical problem may be stated concisely as follows.

Find the variation in hot junction temperature, $(T_{ho} - T_{hf})$, in a system having no power flattening device under the following conditions:

1. All heat flux from the isotopic source flows through the generator. The extraneous heat losses are not significant in the context of this problem.
2. For simplicity, the radiator temperature is taken equal to cold junction temperature and the radiator is assumed to reject heat to a sink at absolute zero.
3. For simplicity, the N and P elements of the generator are taken equal in length.

Let us look at the problem in a qualitative manner. The generator system is designed for a specified power and voltage output at end-of-life. Initially, excess thermal input to the thermocouples raises both hot and cold junction temperatures, the hot junction being raised more than the cold junction so that more heat is conducted through the elements. The cold junction temperature is governed by the fixed radiator area. Thus if the heat conducted is raised 25%, the cold junction temperature (absolute) is increased by about 6%. Also, efficient generator design generally results in the Peltier heat being about one-third the conducted heat at end-of-life. The Peltier heat absorbed at the hot junction is also roughly proportional to the cube of the hot junction temperature. Thus, if the hot junction temperature is 25% greater at start-of-life than at the end-of-life, the Peltier heat is increased about 95%. Therefore, if the total thermal input (sum of Peltier

heat plus conducted heat plus a small Joulean heat contribution) is 48% greater at θ_o than θ_F . There will be an increase of 25% in hot junction temperature at θ_o compared to θ_F .

The exact analysis of the above situation leads to a complicated equation that cannot be made explicit in terms of temperatures but requires iterative solution techniques. For this reason, a simplified approximate analysis was also worked out. It will become apparent that the approximate analysis is sufficiently accurate for the present comparative purposes.

3.1.1 Exact Analysis

With no excess heat dumping mechanism,

$$Q_G = Q_I = Q_P + Q_C + \frac{1}{2} I^2 R_G \quad 3.4.1$$

where $Q_P = N \alpha I T_h$ 3.4.2

$$I = \frac{N \alpha (T_h - T_c)}{R_L + R_G} \quad 3.4.3$$

$$\begin{aligned} R_G &= \left[\left(\frac{\rho L}{A} \right)_N + \left(\frac{\rho L}{A} \right)_P \right] \\ &= \left[\left(\frac{\rho}{A} \right)_N + \left(\frac{\rho}{A} \right)_P \right] NL \end{aligned} \quad 3.4.4$$

The conducted heat is merely

$$Q_C = N (T_h - T_c) \left[\left(\frac{kL}{A} \right)_N + \left(\frac{kL}{A} \right)_P \right] \quad 3.4.5$$

Assuming the cold junction temperature equals the radiator temperature,

$$Q_{G_0} = Q_{I_0} = \epsilon A_R \sigma T_{C_0}^4 + P_0$$

$$Q_{G_F} = Q_{I_F} = \epsilon A_R \sigma T_{C_F}^4 + P_F$$

$$\text{Thus, } T_{C_0} = T_{C_F} \left(\frac{Q_{I_0} - P_0}{Q_{I_F} - P_F} \right)^{1/4} = T_{C_F} \left(\frac{Q_{I_0}}{Q_{I_F}} \right)^{1/4} \quad 3.4.6$$

If we neglect the Joulean heat term $\frac{1}{2} I^2 R_G$ in comparison with Q_I , we obtain from the above in

$$\frac{Q_{I_F}}{Q_{I_0}} = \frac{\left[\frac{N \alpha_F^2 T_{hF}}{R_L + N L \left(\frac{r_{NF}}{A_N} + \frac{p_{PF}}{A_P} \right)} + \frac{K_{PF} A_P + K_{NF} A_N}{L} \right] (T_{hF} - T_{CF})}{\left[\frac{N \alpha_0^2 T_{h0}}{R_L + N L \left(\frac{r_{N0}}{A_N} + \frac{p_{P0}}{A_P} \right)} + \frac{K_{P0} A_P + K_{N0} A_N}{L} \right] \left(T_{h0} - T_{CF} \left\{ \frac{Q_{I_0}}{Q_{I_F}} \right\}^{1/4} \right)} \quad 3.4.7$$

In addition, for maximum thermoelectric efficiency Ioffe gives the following relation between A_N and A_P

$$A_P = \sqrt{\frac{p_{PF} K_{NF}}{r_{NF} K_{PF}}} \cdot A_N = C A_N \quad 3.4.8$$

where $C = \text{a constant}$

Substituting 3.4.8 into 3.4.7 leads to

$$\frac{Q_{I_F}}{Q_{I_0}} = \frac{\left[\frac{N \alpha_F^2 T_{hF}}{R_L + \frac{N L}{A_N} \left(r_{NF} + \frac{p_{PF}}{C} \right)} + \frac{A_N (K_{PF} C + K_{NF})}{L} \right] (T_{hF} - T_{CF})}{\left[\frac{N \alpha_0^2 T_{h0}}{R_L + \frac{N L}{A_N} \left(r_{N0} + \frac{p_{P0}}{C} \right)} + \frac{A_N (K_{P0} C + K_{N0})}{L} \right] \left(T_{h0} - T_{CF} \left\{ \frac{Q_{I_0}}{Q_{I_F}} \right\}^{1/4} \right)} \quad 3.4.9$$

For a given mission in which the ratio Q_{IF}/Q_{IO} is determined as a function of θ_F/h , and the end-of-life generator characteristics are defined, equation 3.4.9 can be solved for T_{ho} by iterative techniques. A sample calculation is given in Appendix 6.2 for a generator having the following characteristics:

Power output = 20 watts, end-of-life

Load voltage = 6 volts

$T_{hF} = 1260$ R

$T_{cF} = 830$ R

$\theta_F/h = 0.75$

Thermoelectric material = Lead Telluride

P type 0.3 Atom % Na, N type .03 Mol % PbI_2 .

The solution obtained was $T_{ho} = 1660$ R. An increase in hot junction of 400 R therefore accompanies a ratio of $Q_{IF}/Q_{IO} = .594$. To interpret this result further, note that if $\theta_F/h = .75$ for Ce-144 fuel, $\theta_F = 213$ days; i.e. a little more than six months mission duration. For a six month mission and no power flattening with this fuel it is apparently necessary to accept a variation in hot junction temperature from 1200 F to 800 F. The corresponding variation in Carnot efficiency turns out to be from 43 to 34% (beginning to end-of-life). The variation in overall thermoelectric efficiency would be about 30% so that the generator must be about 30% "larger" than it would be if thermal power input were constant.

Another way of putting this result is: if the thermoelectric material could operate satisfactorily for six months at the upper temperature level of 1200 F, then the system should be designed to operate at this level throughout the mission in order to give the highest efficiency and lightest weight system.

3.1.2 Approximate Analysis

The work of solving equation 3.4.9 for T_{ho} can be greatly reduced with little loss in accuracy by using the fact that in most lead telluride generators

the Peltier heat equals approximately one-third of the total heat input to the generator. Thus,

$$Q_G = Q_P + Q_C \doteq \frac{1}{3} Q_G + Q_C$$

or
$$Q_G \doteq \frac{3}{2} Q_C$$

3.4.10

Then
$$\frac{Q_{GF}}{Q_{Go}} = \frac{Q_{IF}}{Q_{Io}} = \frac{(CK_{PF} + K_{NF})(T_{HF} - T_{CF})}{(CK_{Po} + K_{No})(T_{Ho} - T_{CF} \left\{ \frac{Q_{Io}}{Q_{IF}} \right\}^{1/4})}$$

3.4.11

Using equation 3.4.11 with the same data as before, and solving for T_{Ho} by the iterative method given in Appendix 6.2 results in $T_{Ho} = 1675$ R. which is less than one percent different than the exact solution. Figure 3.1.1 shows the calculated change in hot junction temperature $T_{Ho} - T_{HF}$ for various values of T_{HF} as a function of θ_F/h .

3.1.3 Conclusion

The above analysis demonstrates that large changes in hot junction temperature characterize the behavior of an RIG system not provided with a power flattening device. A power flattening device that dumps excess heat increases the effectiveness of an RIG system by preventing damaging temperature excursions while at the same time permitting operation at maximum thermoelectric efficiency and minimizing the required radioisotope inventory.

3.2 System Efficiency vs. Relationships

In this section the the mal flows through an idealized power-flattened RIG will be analyzed and a quantitative criterion for judging the performance of the power flattening device will be established. The notation used is illustrated in Figure 3.2.1.

FIG. 3.1.1 CHANGE IN HOT JUNCTION TEMPERATURE FOR AN RTG SYSTEM WITHOUT POWER FLATTENING.

FIGURE 3.2.1

HEAT FLOWS AND TEMPERATURES
IN IDEALIZED RTG SYSTEM.

At all times, $Q_E = Q_I - Q_G$ so that

$$\frac{Q_{EF}}{Q_{E0}} = \frac{Q_{IF} - Q_G}{Q_{I0} - Q_G} = \frac{Q_{I0} \frac{Q_{IF}}{Q_{I0}} - Q_G}{Q_{I0} - Q_G} \quad 3.2.1$$

where we can write Q_G without a subscript because the power flattening device presumably maintains constant heat input to the generator. We will define a "system effectiveness" $= \gamma$ so that

$$\gamma = \frac{Q_G}{Q_{I0}}, \quad 0 < \gamma < \gamma_M \quad 3.2.2$$

where γ_M is a maximum value defined by equation 3.2.5 below. Then from equations 3.2.1 and 2.2.3,

$$\frac{Q_{EF}}{Q_{E0}} = \frac{e^{-.693\theta_F/h} - \gamma}{1 - \gamma} \quad 3.2.3$$

or

$$\gamma = \frac{e^{-.693\theta_F/h} - \frac{Q_{EF}}{Q_{E0}}}{1 - \frac{Q_{EF}}{Q_{E0}}} \quad 3.2.4$$

The maximum value for γ (for an ideal power flattening device) is given when $Q_{EF}=0$, i.e., there is no heat leakage through the power flattening system at end-of-life. Equation 3.2.4 then reduces to

$$\gamma_M = e^{-.693\theta_F/h} = \frac{Q_{IF}}{Q_{I0}} \quad 3.2.5$$

The difference between γ_M and γ is another measure of performance and is given by

$$\gamma' = \gamma_M - \gamma = \frac{Q_{IF} - Q_G}{Q_{I0}} = \frac{Q_{EF}}{Q_{I0}} \quad 3.2.6$$

It is clear that γ and γ' are merely complementary definitions.

As an illustration, if we have a perfect mechanical shutter, Q_{EF} will be zero when the shutter is fully closed at the effective "end-of-life." Then $\gamma = \gamma_M$. If the shutter is less than perfect, $Q_{EF} > 0$ and $\gamma < \gamma_M$. In passing we remark that "end-of-life" in the present connotation merely designates that point in time when $Q_G = Q_I$. For $\theta > \theta_F$ the heat source supplies less than "rated" power.

The full significance of γ as a measure of performance is brought out by a parametric study. We first note that the radioisotope inventory is directly related to γ and is simply $Q_{I0} = Q_G / \gamma$. For example, for $\theta_F/h = 1.0$, Figure 2.2.1 gives $Q_{IF}/Q_{I0} = 0.5$. In this case $\gamma_M = 50\%$ and $(Q_{I0})_{MIN.} = 2Q_G$. Using γ as defined, various power flattening devices can be directly compared for effect on radioisotope inventory.

3.2.1 Effectiveness as a Function of Mission-Life to Half-Life Ratio

Equation 3.2.4 gives γ as a function of Q_{EF}/Q_{E0} and θ_F/h . From the illustrative example of the shutter it is apparent that Q_{EF}/Q_{E0} is a function of the design and construction of the power flattening device; e.g. how perfectly the shutter closes at time θ_F . The θ_F/h ratio is a function only of the selected mission and the chosen radioisotope. These two factors immediately limit the maximum performance of the overall system. This is illustrated in Figure 3.2.2 where γ is plotted against Q_{EF}/Q_{E0} for various values of $e^{-6.93\theta_F/h}$. The asymptotic behavior of γ as Q_{EF}/Q_{E0} decreases shows that little is gained by decreasing Q_{EF} beyond a certain point. For example, for $e^{-6.93\theta_F/h} = 0.5$, γ doubles in value (from 20 to 40%) when Q_{EF}/Q_{E0} halves from 0.375 to 0.15, but only increases 6% when Q_{EF}/Q_{E0} halves from 0.15 to 0.075.

FIGURE 3.2.2

EFFECTIVENESS VS Q_{EF}/Q_{EO}
FOR VARIOUS VALUES OF $e^{-.693\theta_F/h}$

Another important fact displayed in Figure 3.2.2 is the sensitivity of the Q_{EF}/Q_{EO} ratio to variations in θ_F/h . For example, in going from $\theta_F/h = 0.50$ to 0.72 with $\gamma = 50\%$, Q_{EF}/Q_{EO} goes from 0.4 to 0.2 . In other words, the "shutter" in one case has a "turndown" of $10:4$ and in the second case a turndown of $10:2$. The requirements on the shutter are twice as severe as a result of a 50% increase in mission life.

3.2.2 Radiator Area as a Function of Effectiveness

The area of the power flattening or secondary radiator can be related to γ as follows. Let

$$A'_R = \frac{Q_{EO}}{\epsilon \sigma T_R'^4} = \frac{Q_{I_0} - Q_G}{\epsilon \sigma T_R'^4} \quad 3.2.7$$

Substitution of $Q_{I_0} = Q_G/\gamma$ gives

$$A'_R = \frac{Q_G}{\epsilon \sigma T_R'^4} \left(\frac{1-\gamma}{\gamma} \right) \quad 3.2.8$$

For a given system where Q_G , ϵ and T_R' are fixed parameters, A'_R varies as the ratio $1-\gamma/\gamma$ as given in the following table:

γ	1.0	.9	.8	.7	.6	.5	.4	.3	.2	.1
$A'_R \sim \frac{1-\gamma}{\gamma}$	0	.11	.25	.43	.67	.50	1.5	2.3	4.0	9.0

Since radiator weight must be minimized, the hyperbolic variation in A'_R with γ is an important consideration. From the table, a system with

$\gamma = 0.8$ has one-half the secondary radiator area of a system with $\gamma = 0.5$, while a system with $\gamma = 0.4$ requires three times the area of one with $\gamma = 0.5$.

Further applications and interpretations of the γ parameter are best deferred until the discussion of the variable emissivity power flattening system in section 4.6.

4. ANALYSIS OF SPECIFIC POWER FLATTENING SYSTEMS

4.1 Classification

Since a large number of power flattening devices were considered in this program, it was convenient and useful to establish two main classes.

Class I. All heat is rejected through a single radiator. Heat flow is regulated within the TEG by shunting heat around the active, power-producing couples by one means or another.

Class II. A secondary radiator rejects all excess heat. The radiator area, emissivity or effectiveness is varied with time in accordance with the requirement of maintaining constant heat input to the TEG.

Conceivably, any particular RFE may employ Class I and II devices in combination. The properties of the resulting system could be arrived at by superposition and need not be separately discussed in this report.

A simple example of a Class I device is given by the case of a TEG provided with $(N + N')$ thermocouples. At θ_0 , N' of these couples are short-circuited for maximum Peltier heat pumping. At θ_F , $(N + N')$ couples are active in producing electrical power. In this way, the heat flow through the active couples and the hot junction temperature of the TEG is maintained reasonably constant (see section 4.2 and analysis of this concept).

A simple example of a Class II device is the mechanical shutter previously mentioned. In one version of this device, the position of the shutter is regulated by a bellows-operated linkage, the bellows in turn being controlled by a fluid-filled thermostat that senses hot junction temperature. Since this particular device has been described elsewhere [3,4], no further discussion is given in this report.

4.2 Peltier Heat Pump Method

In this Class I device the generator is provided with $(N + N')$ couples (sufficient to obtain the required electrical power output P_F at end-of-life). At start-of-life N' couples

are short-circuited electrically so as to maximize the heat absorbed by the Peltier effect. If the hot junction temperature T_{h0} is somewhat greater than T_{hF} , it is conceivable that the required power output can be attained also at start-of-life; i.e. $P_0 = P_F$. By sequentially switching couples from the short-circuit to active condition during the mission, the power output can be kept reasonably constant and the variation in T_h can be reduced. We will now analyze this hypothesis.

The Peltier heat absorbed at the hot junction is

$$Q_P = N \alpha I T_h \quad \dots 4.2.1$$

The current produced by the generator is

$$I = \frac{E_{oc}}{R_L + R_G} = \frac{\alpha (T_h - T_c) (N + N')}{R_G (m + 1)} \quad \dots 4.2.2$$

where $m = R_L / R_G$

$$R_G = \left[\left(\frac{\rho L}{A} \right)_N + \left(\frac{\rho L}{A} \right)_P \right] (N + N')$$

The heat transferred by conduction through the couples is

$$Q_C = (N + N') \left[\left(\frac{KA}{L} \right)_N + \left(\frac{KA}{L} \right)_P \right] (T_h - T_c) \quad \dots 4.2.3$$

Since $m = 0$ for shorted couples, the Peltier heat absorbed by the shorted couples is

$$Q_{PS} = \frac{N'^2 \alpha^2 T_h (T_h - T_c)}{R_G N / N'} \quad \dots 4.2.4$$

The ratio of generator heat flows at θ_0 and θ_F is

$$\begin{aligned} \frac{Q_{G0}}{Q_{GF}} &= \frac{Q_{I0}}{Q_{IF}} = e^{-.693 \theta_F / h} \\ &= \frac{(Q_P + Q_C + Q_{PS})_0}{(Q_P + Q_C)_F} \quad \dots 4.2.5 \end{aligned}$$

Equations 4.2.1 - 4.2.5 and equation 3.4.6 provide all the data needed to find the variation in T_h as a function of θ_F/h for any particular generator; i.e. a generator whose end-of-life properties are given. The final form of the equation is

$$\frac{Q_{G0}}{Q_{GF}} = \frac{(T_{h0} - T_{CF}) \sqrt[4]{\frac{Q_{G0}}{Q_{GF}}}}{(T_{hF} - T_{CF})} \left[\frac{\alpha^2 T_h N}{R_G} + \left(\frac{KA}{L} \right)_N + \left(\frac{KA}{L} \right)_P \right]_0 \dots 4.2.6$$

If a thermoelectric generator is designed for end-of-life conditions and θ_F/h is given, then equation 4.2.6 can be solved by trial-and-error for T_{h0} in terms of the variable parameter N' . The numerical work is lengthy because the thermoelectric properties α_0 , R_{G0} and K_0 are functions of the unknown T_{h0} . A sample calculation is given in Appendix 6.3. The results of the calculations are shown in Figure 4.2.1 which shows T_{h0} and N as a function of θ_F/h . These results apply for the typical lead telluride generator postulated in section 3.4.1. ($P = 20$ watts at 6 volts, $T_{hF} = 1260^\circ R$, $T_{CF} = 830^\circ R$, $\theta_F/h = 0.75$).

An additional relation for the electrical power outputs at θ_0 and θ_F can be derived.

$$\text{Since } P = \frac{V_c^2}{R_L} = \frac{\left(\frac{m}{1+m} \right)^2 E_{oc}^2}{m R_G}, \quad E_{oc} = N \alpha (T_h - T_c)$$

$$\text{and } \frac{m_0}{m_F} = \frac{R_{GF}}{R_{G0}} = \frac{(N+N') \left[\left(\frac{PL}{A} \right)_N + \left(\frac{PL}{A} \right)_P \right]_F}{N' \left[\left(\frac{PL}{A} \right)_N + \left(\frac{PL}{A} \right)_P \right]_0}$$

$$\frac{P_0}{P_F} = \frac{\left(\frac{m}{1+m} \right)_0^2 \left[N^2 \alpha_0^2 (T_{h0} - T_{CF}) \sqrt[4]{Q_{G0}/Q_{GF}} \right]}{\left(\frac{m}{1+m} \right)_F^2 \left[(N+N')^2 \alpha_F^2 (T_{hF} - T_{CF}) \right]}$$

....4.2.7

FIG. 4.2.1

For ideal power flattening $P_o/P_F = 1$; i.e., the power flattening device does not affect the constancy of the electric power output. This fact and equation 4.2.7 provide a second relation between T_{ho} and N that has been used in obtaining the solution shown in Figure 4.2.1.

The variation in T_{ho} for the illustrated case is 250 R (1560-1310) with the number of active couples going from 46 to 88 from start-to end-of-life. Although this is appreciably less than the 400 R change that occurred in an unregulated system, it is not considered acceptable from efficiency and reliability standpoints. The results of a corroborating experiment reported in section 5.2 are in agreement with theoretical predictions.

Conclusion: This method of power flattening, while feasible, is not recommended due to the excessive variation in hot junction temperature. It has the advantage of high effectiveness since $Q_{EF} = 0$ when all couples are active in power production. By solid state switching techniques, the system can be made to follow the required exponential decay curve of the heat source. However, it may prove difficult to obtain high switching capacity for high power level RTG systems. There is also a decrement in efficiency due to losses in the switchgear.

4.3 By-Pass Generator Method

In this Class I device the hot junction temperature may be held within close limits through the use of thermal shunts that divert excess heat from the radioisotope source to the radiator. As the radioisotope decays, the amount of heat bypassed around the active couples must be decreased. Although the hot junction temperature can thereby be kept constant, the cold junction temperature will vary since with a single fixed radiator a greater amount of heat is rejected at θ_o than at θ_F . The consequent reduction in temperature difference would lead to reduced electric power output for $\theta < \theta_F$ but this is compensated by using extra thermoelectric couples as thermal shunts. The extra couples comprise a by-pass generator connected in electrical series with the main generator, the latter group of couples being optimized for end-of-life. The by-pass couples are sequentially removed by a solid state switchgear from the electrical circuit. They are also removed sequentially from

the thermal path between source and radiator by gradually leaking fluid to space, the fluid providing a heat transfer path between the cold junctions and the radiator in the by-pass generator section of the assembly. A suitable fluid would be helium gas, the conductance of the thermal path being proportional to gas pressure. Effectiveness is potentially quite high since the thermal path can be reduced by orders of magnitude very readily thereby minimizing the end-of-life heat loss Q_{EF} .

The first step in the analysis of this device is to calculate the number and size of couples for the end-of-life generator by the method indicated in Appendix 6.4. In order to determine the number and size of the couples in the by-pass generator, and the sequence of removal of these couples, some simplifying assumptions will be made:

1. With small changes in generator temperature level, it can be assumed that α , ρ and K are constant. More exact analysis requires iteration to include effects of variable properties.
2. The thermal and electrical connections between the by-pass and main generators are assumed to be without losses.
3. Junction temperatures are the same for both generators.

Generator cold junction temperature at θ_0 , is given by equation 3.4.6 which is repeated below.

$$T_{C0} \doteq T_{CF} (Q_{I0}/Q_{IF})^{1/4} \quad \dots 3.4.6$$

The sum of the conducted and Peltier heats in the by-pass generator is (neglecting Joulean heat terms),

$$Q'_C + Q'_P = Q_I - (Q_C + Q_P) \quad \dots 4.3.1$$

where primed terms relate to the by-pass generator and unprimed terms to the main generator. The conducted and Peltier heats are

$$Q_C = N \left[\left(\frac{KA}{L} \right)_N + \left(\frac{KA}{L} \right)_P \right] (T_h - T_c) \quad \dots 4.3.2$$

$$Q_p = N I \alpha T_h$$

...4.3.3

Substituting 4.3.2 and 4.3.3 in 4.3.1 with appropriate subscripts and solving for the A/L ratio for the by-pass thermocouples gives

$$\left(\frac{A}{L}\right)' = \frac{Q_{I_0} - \frac{KA}{L}(T_{h_0} - T_{c_0}) - (N + N')(\alpha I_0 T_{h_0})}{K(T_{h_0} - T_{c_0})}$$

...4.3.4

where $K = \frac{K_N + K_P}{2}$

$$A/L = N(A_N + A_P)/L$$

$$L_P = L_N = L$$

The electric power output at θ_0 is

$$P_0 = \frac{(E_{oc} + E'_{oc}) R_L}{(R_G + R'_{G_0} + R_L)^2}$$

...4.3.5

where $E_{oc} = N\alpha(T_{h_0} - T_{c_0})$

$$E'_{oc} = N'\alpha(T_{h_0} - T_{c_0})$$

Also, we can obtain the by-pass generator resistance as follows, assuming $L_N' = L_P' = L'$,

$$R'_{G_0} = N' \left[\left(\frac{\rho}{A/L}\right)_P + \left(\frac{\rho}{A/L}\right)_N \right]_0$$

Let $(A/L)' = N' \left[(A/L)'_P + (A/L)'_N \right] = \frac{N'}{L'} (A'_P + A'_N)$

For maximum thermoelectric efficiency,

$$A'_N = \sqrt{\frac{\rho_{N'} K_{P'}}{\rho_{P'} K_{N'}}} A'_P = C A'_P$$

where C is a property of the thermoelectric materials.
Combining the above gives

$$R'_G = \left[\rho'_p (1+C) + \frac{1+C}{C} \rho'_n \right] \frac{N'^2}{(A/L)'} \quad \dots 4.3.6$$

Substituting $(A/L)'$ from equation 4.3.4 into 4.3.6 and this result into 4.3.5 results in a quadratic equation solvable for the variable N' .

$$\begin{aligned} \left(\frac{P_0}{R_L} \right)^{1/2} \left\{ R_G + R_L + \frac{\frac{1+C}{C} \rho_p \rho_n K (T_{h0} - T_{c0}) N'^2}{Q_{I0} - K \frac{A}{L} (T_{h0} - T_{c0}) - (N+N')(\alpha I_0 T_{h0})} \right\} \\ = N \alpha (T_{h0} - T_{c0}) - N' \alpha (T_{h0} - T_{c0}) \end{aligned} \quad \dots 4.3.7$$

After N' is computed from 4.3.7, $(A/L)'$ can be computed from 4.3.4. Also, we can obtain

$$(A/L)'_p = \frac{(A/L)'}{(1+C)N'}$$

and

$$(A/L)'_n = \frac{C}{1+C} \frac{(A/L)'}{N'}$$

If we then let $A_p = A'_p$ we can calculate

$$L'_p = L'_n = A_p / (A/L)'_p$$

The remaining problem is to determine the time and sequence of removal of by-pass couples from the thermal and electrical circuits. We define an allowable lower limit of the power output P_u that is produced just prior to the time of the first removal.

$$P_u = \frac{[(N+N')(\alpha)(T_{hu} - T_{cu})]^2 R_L}{[R_G + R'_G + R_L]^2} \quad \dots 4.3.8$$

The sum of the conducted and Peltier heats at time of first removal is

$$Q_{Iu} = \left[\left(\frac{KA}{L} \right) + \left(\frac{KA}{L} \right)' \right] (T_{hu} - T_{cu}) + (N+N')(\alpha I_u T_{hu}) \quad \dots 4.3.9$$

where $I_u = \sqrt{P_u/R_L}$

and $Q_{Iu} = Q_{IF} (T_{cu}/T_{cf})^4 = Q_{I0} e^{-.693\theta_u/h} \dots 4.3.10$

Equations 4.3.8 and 4.3.9 can be solved for T_{hu} and T_{cu} , and 4.3.10 used to compute θ_u . The number of bypass couples to be removed at time θ_u in order to increase the power from P_u to P_o is found as follows:

$$P_o = \frac{(E_{ocu} + E'_{ocu}) R_L}{(R_G + R'_{Gu} + R_L)^2} \dots 4.3.11(a)$$

$$I_u = \sqrt{\frac{P_o}{R_L}} = \frac{(N + N'_u)(T_{hu} - T_{cu}) \alpha}{R_G + R'_{Gu} + R_L} \dots (b)$$

$$R'_{Gu} = N'_u \left[\frac{P_P}{(A/L)'_P} + \frac{P_N}{(A/L)'_N} \right] \dots (c)$$

Equation 4.3.11 a,b,c provide sufficient data to set up an expression giving T_{hu} as a function of N'_u or $T_{hu} = \phi(N'_u)$. Since Q_{Iu} is given by 4.3.9 we can also write

$$\begin{aligned} Q_{Iu} &= Q_{hu} + Q_{pu} + Q'_{hu} + Q'_{pu} \\ &= K \left[\left(\frac{A}{L} \right) + \left(\frac{A}{L} \right)'_u \right] (T_{hu} - T_{cu}) + (N + N'_u) \alpha I_u T_{hu} \end{aligned} \dots 4.3.12$$

Substituting $T_{hu} = \phi(N'_u)$, $I_u = (P_o/R_L)^{1/2}$ and $(A/L)' = N' [(A/L)'_P + (A/L)'_N]$ into 4.3.12 results in a quadratic equation solvable for N'_u . The changes occurring at time θ_u are now completely defined. The above procedure can be repeated to determine the changes occurring until end-of-life.

Appendix 6.4 shows the results of this procedure for the same end-of-life generator postulated in Appendix 6.4.

The power output of the generator fluctuates between 18 and 23 watts. With 13 by-pass couples the hot junction goes from 1480 to 1367 R. at the end of the first switching step. At this point 9 by-pass couples are removed. The second and last step removes the remaining 4 by-pass couples at a time when T_h has reached 1357R.

Conclusion: The advantage of this system is that high effectiveness can be attained since $Q_{EF} = 0$ when all by-pass couples are removed at end-of-life. The disadvantages are (a) that extra couples and a highly efficient, high-capacity switchgear are required, and (b) the use of a fluid heat transfer medium for the path between heat source and by-pass couples adds to the reliability problem. A fairly sophisticated switching control is necessary which would also add to the reliability assurance problem.

4.4 Variable Thermal Contact Resistance

In this Class II system excess heat is diverted to a secondary radiator. The area and emissivity of the secondary radiator are fixed but the thermal conductance between the radioisotope container and the base of the radiator is made to vary in the desired manner. The variation may be achieved by mechanical means, e.g., by providing a thermal contact resistance that varies with the pressure or load on the interface between heat source and radiator base. Thus, if the thermal contact resistance is linearly proportional to interface pressure, then an exponentially varying pressure will result in exponential variation in conductance deviates somewhat from a pure exponential variation.

One method of producing an exponential pressure variation is by using a gas leaking out of an orifice. The gas is confined in a flexible container such as a bellows or piston-cylinder so that the variation in pressure inside the container determines the load on the thermal contact interface.

The required functional variation of thermal contact conductance U_E can be found as follows:

$$U_E = \frac{Q_E}{T_I - T_{R2}} = \frac{Q_I - Q_G}{T_I - \sqrt[4]{(Q_I - Q_G)/\epsilon \sigma A_{R2}}} \quad \dots, 4.4.1$$

This can also be written (since Q_G and T_I are constants),

$$U_E = \frac{\phi_1 (Q_{I0} e^{-.693\theta/h})}{\phi_2 (Q_{I0}^{1/4} e^{-\frac{1}{4}(.613\theta/h)})} \quad \dots 4.4.2$$

The contact conductance is also a linear function of contact pressure p . This has been shown by numerous experiments and has been verified in this program as described in section 5.3. In Appendix 6.8 we also show that the gas leak device results in a pressure-time relationship of the form $p = p_0 e^{-\alpha t}$ so that

$$U_E = \phi p_0 e^{-\alpha t} \quad \dots 4.4.3$$

Comparing 4.4.2 and 4.4.3 we see that the denominator in 4.4.2 will cause some deviation from ideal power flattening. The magnitude of the deviation has been calculated to be less than 10% of electrical power output for $\theta_F/h = 0.75$. An experimental program (described in section 5.3) was conducted which verified the assumptions required for this analysis; the exponential change in gas pressure and the linear variation of interface thermal conductance with pressure. The preceding analysis and the test results indicate that this power flattening method possesses theoretical feasibility. The difficulty of maintaining a properly aligned interface and the problems of maintaining a controlled leak combine to make this method impractical for an actual mission, especially when compared to other methods that can be used.

4.5 Variable Radiator Area

In this Class II device the secondary radiator is composed of a finite number of segments, each of which is ejected into space following a prescribed sequence. The ejection mechanism may take various forms: electrically-ignited explosive squibs; electrically-tripped spring latches; holding solenoids. The mechanism must be capable of service at cold junction temperature levels and in space environment. Also, after a radiator segment is ejected it may tend to expose a part of the generator at high temperature; this heat loss must be prevented by appropriate design and use of low emissivity surfaces on parts that are not ejected.

The analysis that follows was verified experimentally and showed that satisfactory power flattening could be achieved with three radiator ejector sequences for $\theta_F/h = 0.75$.

The analytical problems are to determine the secondary radiator area A'_R , the thermal conductance of the path from heat source to secondary radiator U_E , the times of segment ejection, and the change in A'_R at each stage of ejection.

A'_R is determined at once from the requirement that Q_{E0} is radiated at temperature $T_{R'}$.

$$A'_R = \frac{Q_E}{\epsilon \sigma T_{R'}^4} \quad \dots 4.5.1$$

U_E is determined by the temperature difference between the source T_I and radiator $T_{R'}$.

$$U_E = \frac{Q_E}{T_I - T_{R'}} \quad \dots 4.5.2$$

Then since $Q_E = Q_I - Q_G$,

$$Q_I - Q_G = U_E \left[T_I - \sqrt[4]{(Q_I - Q_G)/\epsilon \sigma A'_R} \right] \quad \dots 4.5.3$$

For ideal power flattening ($Q_G = \text{constant}$) equation 4.5.3 indicates that both U_E and A'_R must be varied continuously with time in a prescribed manner. Since a practical embodiment of this concept involves a finite number of incremental changes a tolerance must be assigned for the variation in Q_G and T_I . We will assume Q_G and T_I each vary by +8%, -5% which results in a +15%, -10% variation in power output. We then define Q'_G , T'_I as lower limits and Q''_G , T''_I as upper limits. Rewriting 4.5.3 for conditions just before the time of the first radiator ejection gives

$$Q_{I_1} = Q'_G + U_{E_0} \left[T'_I - \sqrt[4]{(Q_{I_1} - Q'_G)/\epsilon \sigma A'_{R_0}} \right] \quad \dots 4.5.4$$

where $Q'_G = 0.95 Q_G$, U_{E_0} is given by 4.5.2, $T'_I = 0.95 T_I$

and A_{R_0}' is given by 4.5.1. Thus 4.5.4 can be solved for $Q_{I_1} = Q_{I_0} e^{-0.693 \theta_1 / h}$. The magnitude of the change in A_{R_1}' and U_E at θ_1 is determined by solving the following equation for X , the fraction of U_E and A_{R_1}' remaining after the change. ($X = (U_{E0} - \Delta U_E) / U_{E0}$)

$$Q_{I_1} - Q_{G''} = X U_{E0} \left[T_I'' - \frac{\sqrt[4]{Q_{I_1} - Q_{G''}}}{\epsilon \sigma X A_{R_0}'} \right] \quad \dots 4.5.5$$

Equation 4.5.5 is equation 4.5.3 re-written for conditions just after the first ejection

The above procedure is repeated until end-of-life is reached. The calculations based on this analysis for the end-of-life generator postulated in Appendix 6.4 are given in Appendix 6.7. These calculations show that for $\theta_F/h = 0.75$, three ejection stages are required to limit the variation in power output to +15%, -10%. The test program described in section 5.4 confirmed the analytical findings.

4.6 Variable Radiator Emissivity

In this Class II device the secondary radiator emissivity is made to vary during the mission in a manner consistent with the decay of the heat source. The emissivity variation may be achieved by use of a radiator having a low emissivity, stable base surface covered with a high emissivity coating that sublimates or evaporates at radiator temperature. The cover coating has a variable thickness so that it gradually exposes the low emissivity base coating in accordance with a prescribed schedule. Radiator area and the thermal conductance between source and radiator base are fixed.

The advantages of this method are that the system requires no moving parts or auxiliary controls, is not subject to meteoroid or radiation damage, and can be made very light in weight. There is no apparent limit on the power level capability and the design is such that the parts can be scaled up or down in capacity very readily.

Since emissivity cannot be made exactly zero a certain amount of extraneous heat is lost at end-of-life; i.e. $Q_{EF} > 0$, and the effectiveness is less than maximum, $\gamma < \gamma_M$.

The high emissivity cover coating must satisfy the following criteria:

1. Melting point higher than radiator temperature.
2. High total emissivity so that radiator area and weight are minimized.
3. Acceptable sublimation or evaporation rate. For example, if the maximum coating thickness is fixed by considerations of fabrication and adherence and is in the range .001 to .100 inches, then for a mission of one year duration the corresponding evaporation rate must be in the range .001 to .100 inches per year at radiator temperature.
4. The cover coating must not react chemically or diffuse into the base coating so as to alter the emissivity of the base coating or change the rate of evaporation.
5. Preferably, the cover coating should evaporate according to a simple and predictable mechanism in order to minimize the design and testing efforts and increase reliability.
6. The thermal expansions of both cover and base coatings relative to the radiator itself should be considered. By applying coatings to a pre-heated radiator and on the concave side of a curved radiator, coatings of low thermal expansion can be placed under residual compressive stress which will oppose the thermal stresses due to differential expansion.

The operating temperature of the secondary radiator is an open design choice, the upper limit being somewhat less than the surface of the radioisotope container - that is, about 1400F, and the lower limit being fixed by the desire to minimize radiator weight at about 800F.

The criteria for selecting the base coating are as follows:

1. Low emissivity
2. Compatibility and adherence
3. No chemical reaction or diffusion at operating temperatures.

Experience with metallic coatings has shown that criteria 3 may be difficult to achieve since most metals diffuse readily into one another at temperatures in the range being considered,* For this reason, the radiator itself is selected to be the base emitter for highest reliability assurance and the high emissivity, sublimable cover coating is applied directly to the radiator surface.

The major task in connection with the study of the feasibility of this concept has been to conduct a literature survey of the emissivity and evaporation properties of metals and inorganic compounds potentially suitable for use as a cover coating. Before describing the results of this survey it is necessary to analyze the characteristics of the system in order to define acceptable limits for the emissivity, in accordance with the aim of achieving maximum effectiveness δ .

4.6.1 Effectiveness as a Function of Emissivity Ratio

First, we repeat equation 3.2.4

$$\delta = \frac{e^{-.693\theta_F/h} - (Q_{EF}/Q_{E0})}{1 - (Q_{EF}/Q_{E0})} \quad \dots 3.2.4$$

Now substitute for Q_{EF}/Q_{E0} in 3.2.4

$$\frac{Q_{EF}}{Q_{E0}} = \frac{\epsilon_F}{\epsilon_0} \frac{\sigma \eta_F A'_R T'^4_{RF}}{\sigma \eta_0 A'_R T'^4_{R0}} = \frac{\epsilon_F}{\epsilon_0} \quad \dots 4.6.1$$

for constant radiator efficiency η , area A'_R and base temperature T'_R . This results in

$$\delta = \frac{e^{-.693\theta_F/h} - \epsilon_F/\epsilon_0}{1 - \epsilon_F/\epsilon_0} \quad \dots 4.6.2$$

* It is possible in theory to "saturate" the radiator with a noble metal base coating so that the base coating reaches equilibrium with the radiator. We have no data to verify this idea however.

Figure 4.6.1 calculated from equation 4.6.2 shows δ as a function of $e^{-.693\theta_F/h}$ for various values of the emissivity ratio ϵ_F/ϵ_0 . For $e^{-.693\theta_F/h} = 0.6$ ($\theta_F/h = .72$), the figure shows that 50% effectiveness is attained with $\epsilon_F/\epsilon_0 = .2$ and 43% effectiveness with $\epsilon_F/\epsilon_0 = .3$. Thus if the minimum radiator base emissivity is say $\epsilon_F = .2$, we must have the cover coating emissivity $\epsilon_0 = 1.0$ for $\delta = 50\%$; on the other hand, $\epsilon_0 = 0.67$ for $\delta = 43\%$. It is clear that (since $\epsilon_{\max} = 1.0$) the maximum effectiveness in this case is 50%, but that comparatively little is lost if the emissivity is in a more readily attainable range; i.e. around 0.67. Incidentally, for all cases $\delta_M = e^{-.693\theta_F/h}$ in accordance with equation 3.2.5.

As a further example, consider $e^{-.693\theta_F/h} = 0.5$, so that $\delta_M = 50\%$ and $\theta_F/h = 1.0$. Assume that there is the same limitation on ϵ_F as before, namely $\epsilon_F(\min.) = 0.2$. Now, in order to reach $\delta = 43\%$, Figure 4.6.1 shows that $\epsilon_F/\epsilon_0 = 0.15$. This would require $\epsilon_0 = 0.2/0.15 = 1.33$ which is not possible. We conclude that the variable emissivity concept is most useful for ratios of θ_F/h below about 0.75. Above this value the effectiveness of the system is low, hence the fuel inventory and radiator weight become excessively high.

Finally, let us examine the effect of establishing a criteria that $\epsilon_0 \geq 0.6$ and $\epsilon_F \leq 0.15$, these being readily attainable objectives. Then, by equation 4.6.2, with $\epsilon_F/\epsilon_0 = .25$, we can calculate the items in the following table.

Effectiveness vs. θ_F/h for $\epsilon_0 = 0.6$, $\epsilon_F = 0.15$

θ_F/h	1.0	.8	.7	.6	.5	.4	.2
$\delta_M\%$	50	57	61	65	71	75	87
$\delta\%$	33	43	48	53	61	67	83
$\delta_M - \delta$	17	14	13	12	10	8	4

The term $\delta_M - \delta$ represents the difference between the maximum effectiveness and the actual effectiveness of the system. To illustrate the effect on fuel inventory, consider an ideal system with a radioisotope inventory of 1 lb. with $\delta_M = 0.61$ ($\theta_F/h = 0.7$). With $\delta = 0.48$ from the above

FIGURE 4.6.1

LIMITING VALUES OF γ FOR
CONSTANT AREA $A_F/A_0=1$
AND VARYING ϵ_F/ϵ_0 RATIOS.

$$Q_{IF}/Q_{IO} = e^{-.693 \theta_F/h}$$

table, the radioisotope inventory is increased to $.61/.48 = 1.27$ lbs.

4.6.2 Selection of Cover Coating Material

The requirement for high initial emissivity, $\epsilon_0 \geq 0.6$, limits the choice of cover coating to non-metals and inorganic compounds. A preliminary survey on the basis of emissivity and thermal stability discloses a relatively large number of potentially suitable materials: various titanates, carbonates, sulfides and oxides [7, 8]. Unfortunately, evaporation rates are not readily available or easily calculated for most of these materials. For reference, Table 4.6.1 gives the emissivity and physical properties of some of the materials investigated.

In order to proceed further it is necessary to review the physical chemistry and physics of decomposition and evaporation processes. Only the highlights will be touched upon in this review. The information given here will also be applicable to the power flattening system described in section 4.7.

4.6.3 Evaporation of Metals

The Langmuir equation based on kinetic theory gives the rate of evaporation or sublimation of a pure metal into vacuum. A detailed derivation and discussion of the use of this formula is given in Appendix 6.10. Two equivalent forms are

$$G = 1.85 \times 10^6 \frac{p}{\rho} \left(\frac{M}{T} \right)^{1/2} \quad \dots 4.6.3$$

$$\text{or} \quad W = \frac{\rho G}{12.5 \times 10^6} = \frac{p}{17.14} \left(\frac{M}{T} \right)^{1/2}$$

where

- W = rate of evaporation, gms/cm²/sec
- G = rate of evaporation, cms/yr
- ρ = density of solid metal, gm/cm³
- p = vapor pressure, mm Hg
- M = molecular weight of material in gas phase
- T = temperature, °K

Table 4.6.2 shows the sublimation rates W and G for some relatively volatile elements as a function of temperature. The table is restricted to elements having a melting point

Table 4.6.1 Emissivity and Physical Properties of Potential Cover Coating Materials for Power Flattening by Variable Emissivity

Material	Melt. Point °F	Molecular Weight M	Density ρ gm/cm ³	ϵ @ 800F	ϵ @ 1000F	ϵ @ 1200F	ϵ @ 1400F	Ref.
BaO	>3500	153.36	5.72	High*	-	-	-	8
CaO	4662	56.08	3.40	High	-	-	-	8
CuO	1879 dec.	79.57	6.40	-	.53-.88	-	.66	7
MgO	>4500	40.32	3.65	.58	.55	.50	.47	8
PbO	1630	223.21	9.53	.6	-	-	-	7
Cr ₂ O ₃	3614	152.02	5.21	-	-	-	.87	7
ZnO	~3270	81.38	5.47	High	-	-	-	8
MoO ₃	1450	143.05	4.50	.83	.81	-	-	7
CaTiO ₃	-	135.98	4.10	.91	.92	.92	.93	10
TiO ₂ pver Enamel	2984 dec.	79.90	3.84	High	-	-	-	8
PbCrO ₄	1551			High	-	-	-	8
<u>Radiator Materials:</u>								
Polished silver	1760	107.88	10.5	.05	.05	-	-	7
Polished copper	1980	63.57	8.92	.09	.13	.18	.19	7
Pure aluminum	1220	26.97	2.702	.10	.12	-	-	7
Aluminum, Light oxide	1220	101.94	3.5	.15	.18	-	-	7
λ max, microns	-	-	-	4.13	3.56	3.14	2.80	-

* High emissivity = .8 - .9

λ max = wavelength at which black-body radiation intensity is a maximum for corresponding temperatures.

Table 4.6.2 Calculated Rate of Evaporation for Some Volatile Metallic Elements Potentially Useful in Power Flattening by Variable Base Area Method.

Element	Melting Point °F	Molecular Weight M	Density gm/cm ³	T = 800F (700K)		T = 1070F (850K)		T = 1340F (1000K)	
				p mm.Hg	G* cms/yr	p mm.Hg	G cms/yr	p mm.Hg	G cms/yr
Ag	1761	107.88	10.5	10 ⁻¹⁰	7 10 ⁻⁶	9 10 ⁻⁹	5.7 10 ⁻⁴	3 10 ⁻⁶	.175
Al	1220	26.97	2.70	10 ⁻¹¹	1.2 10 ⁻⁶	3 10 ⁻⁸	3.7 10 ⁻³	3 10 ⁻⁶	liquid
Ba	1562	137.3	3.5	2 10 ⁻⁵	4.9 10 ²	3 10 ⁻³	6.4 10 ³	9 10 ⁻²	1.8 10 ⁴
Ca	1490	40.08	1.55	3 10 ⁻⁵	8.6 10 ²	7 10 ⁻³	1.8 10 ⁴	2 10 ⁻¹	4.8 10 ⁵
Cu	1981	63.57	8.92	10 ⁻¹⁰		2 10 ⁻⁹		9 10 ⁻⁷	
Mg	1204	24.32	1.74	7 10 ⁻³	1.4 10 ³	5 10 ⁻¹	9 10 ⁴	10.0	liquid
Mn	2300	54.93	7.2	10 ⁻¹⁰	7 10 ⁻⁶	8 10 ⁻⁸	.52	2 10 ⁻⁵	1.21
Sb	1167	121.76	6.69	8 10 ⁻⁵	9.3 10 ⁻²	3 10 ⁻²	3.1 10 ³	9.0	liquid
Zn	788	65.38	7.14	2 10 ⁻¹	liquid	9.0	liquid	90.0	liquid

$$* G = 1.86 \times 10^{+6} \frac{p}{e} \left(\frac{M}{T} \right)^{1/2}$$

greater than 750C. For reference, Figure 4.6.2 is included to show vapor pressure vs. temperature of a number of elements.

4.6.4 Evaporation of Alloys

Raoult's law is customarily used to calculate the depression of the vapor pressure of a constituent of an alloy. For example, if an iron-manganese alloy contains 13% Mn and 87% Fe (mol fractions), then as a first approximation,

$$p_{\text{Mn}} = .13 \times \text{Vapor Pressure of pure Mn}$$

$$p_{\text{Fe}} = .87 \times \text{Vapor Pressure of pure Fe}$$

Since all metals have about the same slope on a log-log curve showing vapor pressure versus temperature, the rate of change of evaporation rate with temperature will be about the same for an alloy as for a pure metal. It will become clear in the discussion in section 4.7.4 that the important design parameter for the variable base area system of section 4.7 is the slope of the vapor pressure-temperature curve. This slope determines the profile of the base in that power flattening system. Furthermore, the use of alloys in the variable emissivity system does not lead to any improvement since alloys tend to have low emissivities; i.e., the emissivity of alloys is in the same range as that for pure metals.

4.6.5 Evaporation of Inorganic Compounds

The evaporation of even simple inorganic compounds is a complex process since several mechanisms are possible. First, molecules of the compound may sublime, in which case the Langmuir equation gives the rate of evaporation in vacuo. The major complications in analyzing the sublimation of compounds arise in the prediction or measurement of the vapor pressure, and in the determination of the molecular weight of the species present in the gas phase. Various methods of calculating vapor pressure from free energy data have been developed and results for a large number of compounds are available in the literature.

A very wide range of sublimation rates has been found by a brief search of the literature. However, if we restrict

Fig. 4.6.2
 Vapor Pressure vs Temperature for Common
 Elements in Range of Interest in Power Flattening.

ourselves to materials such as metal oxides, whose emissivity and melting points are in the desired ranges for power flattening, the rates of direct sublimation alone would be found to be too low to be of practical interest.* For example, barium oxide, one of the most volatile, sublimes in the compound form at a rate of only .000855 mm/yr at 1400°F.

Another mechanism in the evaporation of inorganic compounds, that is of even greater importance in power flattening, is the decomposition of the compound to the elements, followed by volatilization of the elements. This may be exemplified by the case of barium oxide. In this case, consider the two reactions, [13]

where ΔF_0 and ΔF_v denote the free energy changes per gram mole BaO or gram atom Ba of the respective reactions. Then, $\Delta F_1 = \Delta F_0 + \Delta F_v$ = free energy per gram mole of BaO of the reaction 4.6.6,

If the reaction is carried out in a volume maintained at temperature T,

$$\Delta F_1 = R_0 T \ln K_1 \quad \dots 4.6.7$$

where the equilibrium constant K_1 is

$$K_1 = P_{\text{atm}}(\text{Ba}) \sqrt{P_{\text{atm}}(\text{O}_2)} \quad \dots 4.6.8$$

and R_0 = universal gas constant
 $= 62.364 \text{ mm. liter deg}^{-1}\text{K g mole}^{-1}$

* One exception has been found among the oxides. Molybdenum tri-oxide (MoO_3) has an exceptionally high vapor pressure, $p = 0.76 \text{ mm.}$ at 726°C (Dushman). This yields an excessive evaporation rate of 118,000 cm/yr; hence MoO_3 is not suitable. Similarly, the chlorides of sodium and potassium have very high vapor pressures at high temperatures which make them unsuitable. For example, NaCl at 592°C evaporates at a rate of 220 cm/yr.

Converting pressure units to mm Hg, and substituting for $P(O_2) = 0.5 P(Ba)$ we obtain, (see Appendix 6.9),

$$\log_{10} P_{mm}(Ba) = 2.982 + \frac{\Delta F_i}{6.861T} \quad \dots 4.6.9$$

As shown by Dushman, the vapor pressure of a metal in equilibrium with solid oxide can be considerably less than the vapor pressure of the solid (or liquid) metal at the same temperature T .

Using the value of the vapor pressure from equation 4.6.9, the rate of evaporation of barium from the surface of the barium oxide can be calculated from the Langmuir equation. The assumption made in this step is that the barium evaporation is the rate-controlling factor, and that the diffusion of barium atoms or ions through the barium oxide to the free surface of the emitter is not a seriously attenuating factor. (It was not within the scope of this program to delve deeply into this question). It may be noted that much work has been done on ionic migration and an excellent introductory discussion may be found in Dushman. It is believed that the assumption made above is reasonably valid for the present problem, although experimental evidence would be desirable.

Finally, an additional evaporation mechanism has been reported [14]. Apparently, in some ceramics, a change of composition can occur within the limits of phase stability as exemplified by the following reaction :

This type of reaction occurs only at temperature levels above our range of interest and is of no practical significance in power flattening.

It became apparent after a few sample calculations, that the governing factor in the evaporation of the inorganic compounds of interest is the two-step process of decomposition to the elements and evaporation of the elements.

Many inorganic compounds such as oxides, carbonates, fluorides and sulfides have fairly high emissivities and melting points and could be considered for use in the variable emissivity power flattening method. In the time

available during this program, a limited review of published data was accomplished. This review was limited to simple compounds having a melting point greater than 1400F (750C) and where some data on emissivity was available.

We have also restricted ourselves to compounds containing only one oxygen or other non-metallic atom per molecules. This is to avoid the complexity of calculation involved in, for example, the dissociation of Fe_2O_3 which takes place in at least two steps,

The results of this materials investigation are shown in Table 4.6.3. A sample calculation is given for barium oxide and cupric oxide in Appendix 6.9.

4.6.6 Discussion of Power Flattening by Variable Emissivity

The effectiveness of the variable emissivity method is severely limited by the lack of sublimable materials of emissivity greater than about 0.6 to 0.8. It is conceivable that special fabrication methods can be used to increase the emissivity to about 0.9. This has been accomplished with certain materials in the past, notably by sandblasting and by making porous, powder metal structures. However, in the absence of more conclusive evidence, we must assume that maximum cover coating emissivity is about 0.8. With a minimum radiator emissivity of about 0.15, the maximum effectiveness of the system is 58% for $\theta_F/h = .75$ ($\delta_M = 66\%$), and 38% for $\theta_F/h = 1.0$ ($\delta_M = 50\%$). Therefore, this system is probably most suitable for $\theta_F/h \leq .75$.

The limitation of the variable emissivity method to the lower range of θ_F/h may be readily overcome through the use of the system described in the next section; namely, the variable radiator base area method that makes use of the same phenomenon of evaporation in space vacuum in a different, more effective manner.

Table 4.6.3 Evaporation Rates of Inorganic Compounds Potentially
Useful for Power Flattening, Calculated at 1000°K (1340F)

Compound	m*	n	Melt. Point °F	Molecular Weight M of Metal	Density of Compound ρ, gm/cc	Vapor Press of Metal P' mm.Hg	$\frac{\Delta F^\circ}{T}$ cal/mole °K	Dissoc- iation Pressure P(M) mm.Hg	Evap- oration Rate G cms/yr	Estimated Range of Utility °Kelvin
BaO	1	1/2	>3500	137.3	5.72	$9 \cdot 10^{-2}$	- 23.00	$9.8 \cdot 10^{-2}$	$1.18 \cdot 10^4$	800-850
BeO	1	1/2	4660	9.02	3.03	$2 \cdot 10^{-8}$	- 7.76	$4.07 \cdot 10^{-5}$	2.38	950-1000
CaO	1	1/2	4660	40.08	3.40	$2 \cdot 10^{-1}$	- 15.26	$1.1 \cdot 10^{-2}$	$5.87 \cdot 10^3$	800-850
CuO	1	1/2	1880) dec	63.57	6.40	$8 \cdot 10^{-9}$	- 16.55	$2.3 \cdot 10^{-5}$	1.69	950-1000
MgO	1	1/2	>4500	24.32	3.65	$1 \cdot 10^{-1}$	- 11.70	1.0	$7.94 \cdot 10^4$	800-250
MnO	1	1/2	3000	54.93	5.45	$2 \cdot 10^{-5}$	- 20.15	$2.63 \cdot 10^{-5}$	3.68	950-1000
MnS	1	1/2	2950	54.93	3.99	$2 \cdot 10^{-5}$	- 24.95	$1.36 \cdot 10^{-4}$	48.5	900-950
PbO	1	1/2	1630	207.2	9.53	$1 \cdot 10^{-2}$	- 27.23	$1.9 \cdot 10^{-4}$	16.9	950-1000
SnS	1	1/2	1620	118.70	6.18	$1 \cdot 10^{-7}$	+ 3.29	$1.5 \cdot 10^{-3}$	156.	900-950
SnO ₂	1	1	1620	118.70	5.08	$1 \cdot 10^{-7}$	-119.77	$1.6 \cdot 10^{-15}$	$2 \cdot 10^{-8}$	> 1400
ZnO	1	1/2	~ 3270	65.38	5.61	$9 \cdot 10^1$	- 16.10	4.92	$4.18 \cdot 10^5$	750-800

5 * m, n as defined in Appendix 6.9

4.7 Variable Radiator Base Area Method

In this Class II device the secondary radiator is attached to the heat source through a material that gradually evaporates when heated in space. The resulting increase in thermal impedance of the secondary path, while the thermal impedance of the primary path between heat source and thermoelectric convertor remains fixed, diverts a decreasing portion of the total heat output to the secondary radiator. By proper design and selection of materials, the system can be made to provide constant source temperature, constant hot junction temperature and constant heat input to the generator.

Figure 4.7.1 shows the major design features of the device and indicates the notation used in the analysis. The advantages of the device are: (a) contains no moving parts or fluids; (b) can be lightweight since secondary radiator emissivity can be high; and (c) can have high effectiveness since Q_{EF} approaches zero when base material has completely evaporated leaving only the supporting skeleton of low conductivity material.

4.7.1 Analysis of Variable Radiator Base Area Method by Method Shown in Figure 4.7.1

The heat conducted through the radiator base is

$$Q_E = \frac{K \bar{A}}{L} (T_I - T_R) \quad \dots 4.7.1$$

where $\bar{A}$ = effective base area
 K = thermal conductivity, assumed constant
 T_I = constant heat source temperature
 T_R = varying radiator temperature (at root of radiator as shown in Figure 4.7.1)

The radiator temperature is related to Q_E by the fourth-power law so that

$$T_R = (C_1 Q_E)^{1/4} \quad \dots 4.7.2$$

where $C_1 = 1/\epsilon \sigma \eta A_R$ = a constant

If the radiator base is divided into n equal increments of length, each increment being ΔX in length and A_n in cross-sectional area, the thermal impedance of the base is

FIG 4.7.1

FIRST VERSION OF POWER FLATTENING BY
VARIABLE RADIATOR BASE AREA METHOD

$$R = \frac{T_I - T_R}{\sum \frac{K A_n \Delta T_n}{\Delta x}} \quad \dots 4.7.3$$

where A_n = continuous function of the length X . The effective area is therefore

$$\bar{A} = \frac{\sum A_n \Delta T_n / \Delta x}{T_I - T_R} \quad \dots 4.7.4$$

Solving for $\bar{A}$ in equation 4.7.1 yields

$$\bar{A} = \frac{L Q_E}{K [T_I - (C_1 Q_E)^{1/4}]} \quad \dots 4.7.5$$

The required variation of Q_E with time for $Q_G = \text{constant}$ is simply

$$Q_E = Q_I - Q_G = Q_{I_0} e^{-.693 \theta / h} - Q_G \quad \dots 4.7.6$$

If a system effectiveness $\gamma = Q_G / Q_{I_0}$ is part of the given specifications for a postulated mission then 4.7.5 and 4.7.6 completely define the time variation of $\bar{A}$ required for ideal power flattening.

$$\bar{A} = \frac{Q_G L}{K} \frac{\frac{e^{-.693 \theta / h}}{\gamma} - 1}{T_I - [C_1 (\frac{e^{-.693 \theta / h}}{\gamma} - 1)]} \quad \dots 4.7.7$$

However, if we now observe that the rate of evaporation is a function of T_I and T_R , it becomes clear that in order to satisfy equation 4.7.7 the profile of the base; i.e. the x -variation in A_n , will have to be adjusted. In effect, the initial profile of the base must be such that the varying rates of evaporation along the length of the base (L) causes the effective area $\bar{A}$ (given by 4.7.4) to vary with time in accordance with 4.7.7. This represents a non-linear, dynamic system, whose exact numerical solution is beyond the scope of the present program. An approximate analysis will be given that will demonstrate the feasibility of the concept as a practical solution to the power flattening problem.

The relation between base area and rate of evaporation is found using Langmuir's formula,

$$W' = \frac{p \Delta S_n}{17.14} \left(\frac{M}{T} \right)^{1/2} \quad \dots 4.7.8$$

where W' = rate of evaporation in gms/sec from an incremental surface area ΔS_n

and the other symbols have been defined in section 4.6.3. The vapor pressure p is a function of temperature (T) usually of the form $\log p = \alpha - \beta/T$. Equation 4.7.8 can be written

$$W' = \psi \Delta S_n \quad \dots 4.7.9$$

where $\psi = \frac{p_n}{17.14} \left(\frac{M}{T} \right)^{1/2}$ is a known function of the materials selected.

Assuming that the base is circular in cross-section,

$$\Delta S_n = \pi D_n \cdot \Delta x = \sqrt{4\pi A_n} \Delta x \quad \dots 4.7.10$$

The weight of any small section is $W_n = \rho A_n \Delta x$ so that the evaporation rate (the time derivative of W_n) can be expressed as a rate of change of area.

$$W' = - \frac{d(\rho A_n \Delta x)}{d\theta} = - \rho \Delta x \frac{dA_n}{d\theta} \quad \dots 4.7.11$$

Combining 4.7.9, 4.7.10 and 4.7.11 gives an expression relating A_n and time,

$$A_n^{-1/2} \cdot dA = - \frac{\sqrt{4\pi}}{\rho} \psi d\theta \quad \dots 4.7.12$$

For any given initial base profile, T at any section is a determinate function of θ . Therefore, it is possible to integrate equation 4.7.12 and obtain the time variation of the cross-section area for a particular incremental length.

$$\sqrt{A_\theta} = \sqrt{A_0} - \frac{\sqrt{\pi}}{\rho} \int_0^\theta \psi d\theta \quad \dots 4.7.13$$

Consider the extreme end increment of the base nearest the radiator. Since this is the coldest part of the base, the "end-of-life" condition, insofar as the power flattening device is concerned, occurs when the area of this part of the base is reduced to the skeletal supporting structure, or approximately when $A_{\theta_F} = 0$.

Also, at this section base temperature T equals radiator temperature T_R , where T_R is a known function of time. That is, by 4.7.2 and 4.7.6,

$$T_R^4 = C_1 Q_G \left(\frac{e^{-.693\theta/h}}{\delta} - 1 \right) \quad \dots 4.7.14$$

Substituting $A_{\theta_F} = 0$ in 4.7.13 yields,

$$\sqrt{\frac{A_0}{\pi}} = \frac{1}{e} \int_0^{\theta_F} \psi d\theta \quad \dots 4.7.15$$

ψ is a complicated function of T_R so that the solution of 4.7.15 for A_0 entails a numerical integration which can be set up in a tabular form:

θ	θ/h	T_R^4 eq. 4.7.14	T_R	ψ eq. 4.7.9	$\psi \Delta\theta$
0					
⋮					
θ_F					
					$\sum \psi \Delta\theta = e \sqrt{\frac{A_0}{\pi}}$

As a first approximation, the material selected for the base should have an evaporation rate such that A_0 turns out to be in the range 0.1 to 0.3 times the desired radiator area. This will give a reasonably high radiator efficiency. The radiator efficiency can be calculated by the method given by Chambers and Somers [27] .

The numerical work needed to determine the exact initial profile of the base for ideal power flattening is beyond the scope of the present program. The necessary procedure is as follows:

1. Assume a trial profile A_0 as a function of x .
2. Calculate the effective area $\bar{A}_0$ by 4.7.4 and the heat flow Q_{E0} by 4.7.1. This will enable the calculation of the temperature at each section of the base.
3. Knowing the temperature at each section, calculate the initial rate of sublimation w'_0 from 4.7.8.
4. Assume the rate of sublimation is constant for a time interval $\Delta\theta_1$. Calculate the base profile at each section at the end of the interval.
5. Repeat the determination of the effective area $\bar{A}_1$, heat flow Q_{E1} , and temperature distribution.
6. Compare Q_{E1} against the ideal value of Q_E at θ_1 from 4.7.6. If there is a large discrepancy, change the initial base profile to reduce the discrepancy.
7. Repeat the above procedure until the base material has completely evaporated or until it becomes apparent that further adjustment of the initial base profile would not reduce the discrepancy between Q_E (actual) and Q_E (ideal). This will determine the time θ_F at which the power flattening device becomes less than ideal. By using the values of Q_E (actual), the deviation in generator power output and hot junction temperature at any time can be calculated.

4.7.2 Calculation of A_0 for an Illustrated Case # 1

Radiator base material is assumed to be pure manganese having the following properties at 1000°K.

Molecular Weight, M	54.93
Density, ρ	7.2 gms/cm ³
* Thermal Conductivity, K	18.2 Btu/hr-ft°F

* No data for the thermal conductivity of manganese above 100°K is available. The value listed is that for iron at 1000°K as a first approximation.

The vapor pressure-temperature relation is given in Figure 4.7.2.

Assume that

$$\begin{aligned} Q_G &= 1000 \text{ watts} \\ h &= 162 \text{ days} \\ \gamma &= \gamma_M = .50 \text{ (50\%)} \\ \epsilon &= .90 \\ \eta &= .75 \text{ (fin efficiency)} \\ \sigma &= .1713 \times 10^{-8} \end{aligned}$$

From the definition $\gamma = Q_G/Q_{I_0}$ we readily obtain

$$Q_{EO} = Q_G \left(\frac{1}{\gamma} - 1 \right) = 1000 \left(\frac{1}{.5} - 1 \right) \times 3.415 = 3415 \frac{\text{Btu}}{\text{hr}}$$

For $T_{R_0} = 1000 \text{ K} = 1800 \text{ R}$, equation 4.7.2 gives

$$C_1 = \frac{T_{R_0}^4}{Q_{EO}} = \frac{1800^4}{3415} = 3.08 \times 10^9$$

Also,

$$A_R = \frac{1}{C_1 \epsilon \sigma \eta} = \frac{1}{3.08 \times 10^9 \times .90 \times .1713 \times 10^{-8}} = .211 \text{ ft}^2 \approx 6 \frac{1}{4} \text{ ins. diameter}$$

Therefore, from equation 4.7.14,

$$T_R^4 = C_1 Q_G \left(\frac{e^{-.693 \theta/h}}{\gamma} - 1 \right) = 1800^4 \left(\frac{e^{-.693 \theta/h}}{.50} - 1 \right)$$

Also, ψ is given by equation 4.7.9.

$$\psi = \frac{p}{17.14} \left(\frac{M}{T} \right)^{1/2} = \frac{p}{17.14} \left(\frac{54.93}{T_R} \right)^{1/2} = .432 \frac{p}{T_R^{1/2}}$$

The calculation of A_0 is shown in Table 4.7.1. Note that the case illustrated is for maximum effectiveness; i.e., $\gamma = \gamma_M = e^{-.693 \theta/h} = .50$; $\theta_F/h = 1.0$.

Table 4.7.1 Calculation of Initial Base Area A_0 for
Illustrative Case # 1

θ days	θ/h	$\frac{C_p - 1}{C_p}$	$T_R, ^\circ R$	$p^*, \text{mm Hg}$	ψ	$\psi \Delta \theta$
0	0	1.0	1800	2.02×10^{-5}	2.04×10^{-7}	$\text{Area} = \frac{1}{2} (2.04) (32) (10^{-7}) = 32.6 \times 10^{-7}$ $\int \psi d\theta = 32.6 \times 10^{-7} \times 24 \times 3600 \text{ sec/day} = .282$
16	.1	.866	1740	8×10^{-6}	$.83 \times 10^{-7}$	
32	.2	.740	1670	1×10^{-6}	$.106 \times 10^{-7}$	
65	.4	.514	1520	8×10^{-8}	$.0085 \times 10^{-7}$	
97	.6	.320	1350	1×10^{-9}	$.000118 \times 10^{-7}$	
129	.8	.148	1120	8×10^{-12}	$.001035 \times 10^{-10}$	
146	.9	.070	925	1×10^{-13}	$.00142 \times 10^{-12}$	
162	1.0	0	0	0	0	

$$\sqrt{\frac{A_0}{\pi}} = \frac{1}{e} \int \psi d\theta = \frac{.282}{7.2} = .0392$$

or $A_0 = .00482 \text{ cm}^2$ equivalent to 0.8 mm diameter.

4.7.3 Calculation of Effective Area at Start-of-Life for Illustrative Case # 1

Assume: L = length of base = 2.54 cm. = .0834 ft.
 $T_I = 1600^\circ \text{F} + 460 = 2060^\circ \text{R}$
 $Q_{E_0} = Q_G = 341.5 \text{ Btu/hr.}$
 $C_1, Q_{E_0} = (1800)^4$

From equation 4.7.5,

* From Figure 4.7.2

FIG. 4.7.2

VAPOR PRESSURE VS. TEMPERATURE FOR MANGANESE

$$\bar{A}_{\theta_0} = \frac{L Q_{E0}}{K[\bar{T} - (C Q_{E0})^{1/4}]} = \frac{.0834 \times 3415}{18.2[2060 - 1800]} = .034 \text{ ft}^2 = 4.90 \text{ in}^2$$

This is equivalent to an "average" diameter of 2 1/2 inches. Comparing this with the value of 0.8 mm diameter (.0315 inches) found for the diameter of the section nearest the radiator, we see that the base must be very sharply tapered. Indeed, as a first approximation, we can estimate that the base diameter at the section nearest the fuel container will be about 3 1/2 to 4 inches.

4.7.4 Discussion and Conclusions

The results of the illustrative Case #1 can be summarized as follows: for $\theta_F/h = 1.0$, with pure manganese as the evaporative base material, ideal power flattening (i.e., maximum effectiveness δ_M) is theoretically attainable with a base configuration approximately as shown below:

Figure 4.7.3 Power Flattening by Variable Base Area, First Version, Showing Base Profile for $\theta_F/h = 1.0$

The reason for the very rapid change in area of the manganese should not be surprising when one considers that the rate of evaporation of the manganese changes by more than one order of magnitude for each change of about 100°R in temperature. The same rate of change will apply to most other metals as well as to metallic alloys as is evident from the vapor pressure curves given in Figure 4.6.2.

It is possible to modify the shape of the profile so as to obtain one that changes more gradually and is therefore, less sensitive to the effects of unavailable deviations from theory. For example, by using the oxide of a relatively volatile metal (instead of a pure metal) the rate of decomposition of the oxide compound to the elements can be made the rate-controlling factor. That is, the vapor pressure of the metallic element as it is dissociated from the compound can be much less than the vapor pressure of the same element over the solid metal. It would be necessary to find a material that changed fairly slowly in free energy with changing temperature in the temperature range of interest for power flattening.

Another possibility is to modify the required profile by diluting the evaporating metal with an inert, refractory filler. For example, manganese powder could be distributed in a prescribed concentration gradient in a matrix of a low thermal conductivity ceramic which has sufficient porosity to allow the manganese to evaporate. The concentration of manganese would be highest in the area next to the fuel container and least in the area next to the radiator, but the part can be arranged to be uniform in diameter. Of course, the mechanism described is much more complicated theoretically than the simple mechanism initially postulated. Experimental adjustments and verifications are required, as well as additional analysis based on firmed-up experimental data.

In response to the complications encountered in the above analysis, a second version of the variable base area method was conceived and is described in the next following section.

4.7.6 Analysis of Power Flattening by Variable Base Area Methods Shown in Figures 4.7.4 and 4.7.5

In the second and third versions of the variable base area method, as shown in Figures 4.7.4 and 4.7.5, the evaporation of material located between the hot extension and the

FIGURE 4.7.4

SECOND VERSION OF VARIABLE RADIATION BASE
AREA POWER FLATTENING METHOD,

FIGURE 4.7.5

THIRD VERSION OF VARIABLE RADIATOR BASE AREA POWER FLATTENING METHOD. EVAPORATION FROM OPPOSITE ENDS TENDS TO CANCEL OUT RECOIL PRESSURE DUE TO THE EVAPORATION.

the radiator hub gradually reduces the thermal conductance of the path. The thickness profile of the evaporating material should be determined so as to yield a variation in thermal conductance consistent with heat source decay. For example, in Figure 4.7.4, it is evident that the thickness of the evaporant will be greatest at the mouth, so that the most rapid changes in heat transfer occur at the beginning of life.

The heat flow through the evaporating material is given by

$$Q_E = \sum_0^n \frac{K 2\pi \Delta x \cdot \Delta T_h}{\ln r_2/r_1} \quad \dots 4.7.16$$

As shown by McAdams, for the case where r_2/r_1 is less than two, the arithmetic-mean area gives an answer accurate within 4% of the exact answer given by use of the log-mean area. Equation 4.7.16 therefore simplifies to

$$Q_E = \sum \frac{K A_m \Delta T_h}{r_2 - r_1} \quad \dots 4.7.17$$

where A_m = mean area of section of length Δx
 $= \pi (r_2 + r_1) \Delta x$

If we assume constant thermal conductivity and substitute the value of Q_E from 4.7.6 into 4.7.17 we obtain for n sections,

$$Q_E = Q_{I_0} e^{-.693\theta/h} - Q_G = \frac{\pi K L}{n} \sum \left(\frac{r_2 + r_1}{r_2 - r_1} \right) \Delta T_h \quad \dots 4.7.18$$

As a first approximation we may assume constant temperature difference across the evaporant, or $\Delta T_h = T_{r_2} - T_{r_1} = \Delta$ constant. But T_{r_2} equals radiator temperature T_R , which is given by equation 4.7.14. If we let r_1 be constant and write r_2 as a function of x , i.e. $r_2 = \phi(x)$, equation 4.7.18 can be written

$$\int_0^{\frac{L}{2}} \frac{\phi + r_1}{\phi - r_1} dx = \frac{Q_{I_0} e^{-.693\theta/h} - Q_G}{2\pi K (T_R - T_{r_1})} \quad \dots 4.7.19$$

In 4.7.19, L and T_R are functions of θ . Since there is no obvious symmetry between the two sides of equation 4.7.19,

it would be difficult to guess the exact form for ϕ that would satisfy the equation. Therefore, even though the physical situation in this case is simpler than that of the first version of the variable base area method, the analytical solution is still very complicated. One method of obtaining a satisfactory design would be to assume some simple forms for ϕ , and compute the corresponding variation of Q_E with time using equation 4.7.9 to determine the variation in L with time. The form of ϕ could then be adjusted for optimum fit to equation 4.7.19.

Because of limited time, and the extreme length of the calculations involved, a numerical solution of the above equations has not been attempted in this feasibility study program. However, since a wide range of evaporation rates is available with common inorganic compounds, and even elemental substances such as manganese, there appears to be no serious theoretical limitation on this method. This method is also apparently suitable for values of θ_F/h , for which other power flattening devices have proven relatively ineffective.

4.8 Variable Thermal Conductivity Method

In principle, the heat input to the TEG and the hot junction temperature can be maintained relatively constant if the thermal conductivities of materials placed between heat source and generator and between source and secondary radiator varied with temperature in the required manner. Referring to Figure 4.8.1, if the material denoted K_2 has a thermal conductivity that increased with decreasing temperature of the source and the material on the opposite side of the source, denoted K_1 , had a conductivity that decreased with decreasing temperature then it is conceivable that the excess heat from the radioisotope source would be distributed as required.

In this Class II device the intention is to find materials having wide variations in thermal conductivity with temperature so that a simple, static regulating mechanism is attained. It is essential that both materials, K_1 and K_2 , be provided. A temperature sensitive material on one side of the source only will not provide power flattening as shown by the following argument:

1. Consider a temperature sensitive member between the source and secondary radiator and assume the hot

FIG. 4.8.1 NOTATION FOR VARIABLE THERMAL CONDUCTIVITY METHOD.

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junction coupled directly to the heat source. The hot junction temperature will remain constant if the source temperature is constant.

2. Consider the secondary thermal path, source to secondary radiator, as diverting all the source heat output not required to maintain the convertor hot junction at a constant temperature to the secondary radiator.
3. If this thermal path could be varied in a suitable manner, the source temperature could remain constant even with variations in source heat output.
4. However, because it is required that source temperature be constant it is not possible to passively vary the source to secondary radiator member in a temperature dependent manner.
5. On the other hand, if the temperature sensitive member were placed between the source and the generator then, if this member could be made to vary in a suitable manner, the hot junction could remain constant while the source temperature varied dependent upon radioisotope decay.
6. For a mission time/half life ratio of 0.75 the excess heat to be rejected is 40% of the total heat at the start-of-life.
7. A thermal path capable of rejecting this 40% must be present at the start-of-life.
8. Since the above thermal path will be present at the end-of-life a proportional amount of heat will be rejected through the secondary path at that time. This results in a very low system efficiency.
9. This demonstrates the need for a variable secondary path and a variable primary thermal path operating simultaneously.

The only special notation used in the analysis of this device is as follows:

K_1 = thermal conductivity of material between source and secondary radiator

K_2 = thermal conductivity of material between source and thermoelectric generator

$(A/L)_1$ = shape factor, source to secondary radiator

$(A/L)_2$ = shape factor, source to generator

Since $QE = K_1 (A/L)_1 (T_I - T_R)$

$$\frac{Q_{E0}}{Q_{EF}} = \frac{K_{I0}(T_{I0} - T_{R0})}{K_{IF}(T_{IF} - T_{RF})} = \frac{T_{R0}^4}{T_{RF}^4} \quad \dots 4.8.1$$

For any material K_1 can be expressed as a function of T_I and T_R and equation 4.8.1 solved for T_{R0} for a case where T_{RF} , T_{I0} and T_{IF} are given parameters. Then the ratio Q_{E0}/Q_{EF} follows from the fourth-power relation. Q_{EF} can then be found by the relations

$$Q_{EF} = Q_{IF} - Q_G$$

and $Q_{IF} = Q_{I0} e^{-.693 \theta_F / h}$

The variation in Q_G is found by assuming constant T_h so that

$$\frac{Q_{G0}}{Q_{GF}} = \frac{K_{20}(A/L)_2 (T_{I0} - T_h)}{K_{2F}(A/L)_2 (T_{IF} - T_h)} \quad \dots 4.8.2$$

The ratio of Q_{G0}/Q_{GF} is an index of the performance of the device and can be calculated for various values of T_h .

Several specific cases are calculated in Appendix 6.6 using beryllia for material K_2 and Fiberfrax for K_1 . The results are not satisfactory for all cases studied because the selected materials did not have sufficiently sharp changes in thermal conductivity with temperature. Fiberfrax and beryllia were selected as materials having the sharpest changes. For satisfactory results, it is estimated that materials would be required that change five to ten times faster than the materials analyzed.

5. EXPERIMENTAL PROGRAM

5.1 Summary

Three of the power flattening devices described in section 4 have been tested. The variable thermal contact resistance method (section 5.3) did not prove satisfactory although the method of theoretical analysis was essentially verified. The Peltier heat pump method (section 5.2) also did not regulate hot junction temperature to a sufficient degree to be considered acceptable. However, the variable radiator area method (section 5.4) proved to be successful in that it provided satisfactory regulation of power output and hot junction temperature. It was not within the scope of the present program to test the variable emissivity device (section 4.6) or the variable radiator base device (section 4.7) since either of these techniques would require elaborate high vacuum, cryogenic type test facilities.

5.2 Peltier Heat Pump Method Test

An experiment was conducted in order to demonstrate the principle of power flattening by the Peltier heat pump method as discussed in section 4.2 of this report.

The experimental generator consisted of ten thermoelectric couples made of P and N bismuth telluride alloys soldered to nickel hot straps and copper cold straps. These couples were selected because of cost, availability and ease of handling. Chromel-alumel thermocouples measured temperatures at both the hot and cold straps. The cold sides of the couples were water cooled with the water flow to each couple individually regulated for uniform cold side temperature. The hot straps of each couple were spring loaded against an electrically insulated hot surface. The spring load on each couple was individually adjustable so that uniform hot side temperature could be attained.

An electrical resistance heater supplied heat to the hot junctions. The 60 cycle a-c. input to the heater was from a voltage regulated source. Two variable transformers were connected in series to regulate the voltage input. The input power was measured with a precision voltmeter and precision ammeter. The electrical heater and hot surface assembly were embedded in Min-K* insulation and Santocel**

* Trade name, Johns Manville Co.

** Trade name, Monsanto Chemical Co.

powder was used to thermally insulate the thermogenerator.

Figures 5.1 and 5.2 are, respectively, a schematic drawing and a photograph of the test setup.

The first step in the test was to measure the Seebeck voltage, E_{oc} , and the resistance of each thermocouple at various hot junction temperatures over the range 700-860°R with a cold junction temperature of approximately 540°R.

The next step was to connect all of the thermocouples in series across a fixed resistive load with the hot junctions at 760°R and the cold junctions at 540°R. The power input, power output across the load, closed circuit voltage, open voltage, hot junction temperature and cold junction temperature were measured.

One of the ten thermocouples was then shorted for maximum Peltier pumping by placing a jumper across the power leads for that particular thermocouple as close to the cold junction as possible. The input power was then increased until the power output across the fixed load was the same as that with all ten couples in series. The measurements referred to above were then repeated.

This procedure was repeated for 2, then 3, and then 4 thermocouples shorted out.

Results

The results of the experiment are in excellent agreement with the theoretical analysis developed in section 4.2.

The purpose of the experiment was, briefly, to evaluate a power flattening technique using a variable number of thermocouples for power generation and to put all thermocouples not needed for power generation in the short circuit mode for maximum Peltier heat pumping. In this way the difference in hot junction temperature over the operating period can be reduced.

Constant electrical power output was obtained over a mission time/half-life ratio of 0.75 by successively changing the active thermocouples from 6 to 10. The hot junction temperatures changed from 750 to 850R as a consequence of the procedure used.

SCHEMATIC-TEST RIG-POWER
FLATTENING BY VARIABLE
Peltier HEAT PUMPING.
FIG. 5.1

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FIG. 5.2

The test results are plotted versus the calculated results on Figure 5.3. The discrepancies between the test and calculated data can readily be explained by the fact that it was not possible to obtain perfect short circuiting of the Peltier couples.

This method of power flattening by the switching of power generating and heat pumping thermocouples is thus demonstrated as feasible and the validity of the analysis is confirmed. However, although feasible, this method of power flattening is not recommended for use in an operational space power supply due to the fact that a 250F variation in hot junction temperature occurs in the illustrative case. While this variation is far better than the 400F change experienced in an unflattened generator, it is still excessive from the standpoint of efficiency and reliability.

5.3 Variable Thermal Contact Resistance Test

This Class II power flattening device in which excess heat is shunted from source to secondary radiator, was analyzed in section 4.4. It was demonstrated there that an exponentially decaying conductance would conduct the excess heat developed at any time, the net result being to maintain the heat flow through the generator at a constant value (also keeping the hot and cold junction temperatures constant). It was shown that the excess heat path interface conductance would decay exponentially for an exponentially decreasing contact pressure provided that the interface conductance was directly proportional to the interface pressure. It was also shown that, theoretically, the gas pressure within a bellows (and the external pressure exerted by the bellows on the interface) should decay exponentially with time if the gas leaks out of the bellows through an orifice and if the gas temperature is constant.

The purpose of the experiment is to verify the two basic assumptions which are essential to the operation of the system, namely; (1) the gas pressure in the bellows (and external pressure exerted by the bellows on the thermal interface of the excess heat path) decays exponentially with time; and (2) the interface conductance varies in direct proportion to the contact pressure.

A test apparatus was set up as shown in figure 5.4. The

HOT JUNCTION TEMPERATURE, T_{hi}
 AND
 NUMBER OF GENERATOR THERMOCOUPLES, N_G
 VS.
 MISSION TIME/HALF-LIFE RATIO, θ_f/h
 FOR
 PROOF OF PRINCIPLE EXPERIMENT
 OF
 PELTIER PUMPING POWER FLATTENING
 WITH
 BOTH EXPERIMENTAL AND CALCULATED
 RESULTS.

FIG. 5.3

SCHEMATIC DRAWING:
TEST RIG FOR DETERMINATION
OF GAS LEAK RATE AND
RESPONSE OF THERMAL
INTERFACE TO PRESSURE.

FIG. 5.4

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bellows and ancillary members are surrounded by Min-K* insulating brick and Santocel** insulating powder. When gas is admitted to the bellows, the flexibility of the bellows permits the bellows to expand longitudinally. This expansion is prevented from occurring since the bellows bears against the interface. The internal pressure, therefore, is transmitted to the interface as an external force.

The procedure used in the determination of the rate of gas leakage is to admit gas to the bellows until a certain pressure is reached (120 psig). Then the gas supply is cut off, and the orifice opened. Readings are taken of gas pressure in the bellows versus elapsed time, and are continued until zero pressure is obtained. This data is then plotted on semi-log paper, and if the decay of pressure with time is exponential, the curve should be a straight line. It was shown in section 6.8 of this report that the exponential decay of pressure with time is predicated on the mass rate of flow of the gas through the orifice being directly proportional to the gas pressure, which is the case for critical flow. Critical flow occurs when the downstream pressure is less than or equal to the critical pressure (as would be the case in space flight). For the present case, which may be considered as adiabatic or isentropic flow having zero velocity of approach, the critical flow pressure for argon (and many other gases) equals about one half the upstream pressure. Therefore, for critical flow to occur, the downstream pressure must be less than or equal to about one half the upstream pressure, or conversely, the upstream pressure must be at least twice as large as the downstream pressures. Since for this experiment the downstream pressure was atmospheric (14.7 psia), the gas pressure must be greater than 29.4 psia (about 15 psig) for critical flow to occur, and the semi-log curve of pressure vs. time should be linear only for pressures greater than 15 psig.

The variation of interface conductance with pressure can be determined by observing the temperatures that occur across the interface for a constant heat input and varying interface pressures. At any pressure level:

* Trade name, Johns Manville Co.

** Trade name, Monsanto Chemical Co.

$$h_c = \frac{Q}{A \Delta T}$$

where

h_c	=	interface conductance, BTU/hr-ft ² -°F
Q	=	heat input (constant), BTU/hr
A	=	interface Area, ft ²
ΔT	=	temperature difference occurring across interface, °F.

These values of h_c versus pressure are plotted on regular graph paper. If the curve that results is linear, then it would be verified that the interface conductance decreases linearly with pressure.

Results

The test described above was conducted and the results verify the two assumptions taken in the section 4.4 analysis; the curve of pressure versus time is exponential and the curve of interface thermal conductance versus pressure is linear. The results are graphically depicted in Figures 5.5 and 5.6.

The curve of pressure versus time is plotted on semi-log coordinates where an exponential relationship should be a straight line. Because the analysis yielding an exponential relationship was based on critical flow, achievable at all times in space, the nature of the curve in Figure 5.5 changed for pressures less than 15 psig when the flow became sub-sonic.

In order to obtain linear, reproducible values of interface thermal conductance it was found necessary to give considerable attention to problems of alignment, flatness, surface finish, etc. Even then it was found that reliable results could not be obtained at pressures below ten psi.

Subsequent to obtaining the data discussed above, it was decided to modify the apparatus as shown in Figure 5.7 so as to add a member analogous to a thermoelectric generator. The purpose of this modification was to gain a better understanding of the overall operation of a gas leak power flattening system. The results were unsatisfactory because the thermal resistance of the variable interface was too

GAS LEAK RATE
GAS PRESSURE VS.
ELAPSED TIME
FOR ARGON LEAKING
FROM ORIFICE ATTACHED
TO BELLOWS

GAS PRESSURE (PSIG)

FIG. 5.5

$$Q = h_c A (\Delta T)$$

$$200 \text{ WATTS} \times 3.42 \frac{\text{BTU}}{\text{hr-watt}} = h_c \left[\frac{(1.414)^2}{4} \right] (\Delta T)$$

$$\text{WHENCE } h_c = \frac{62,600}{\Delta T} \frac{\text{BTU}}{\text{hr-ft}^2\text{-}^\circ\text{F}}$$

FIG. 5.6

SCHEMATIC DRAWING: MODIFIED
TEST RIG FOR POWER
FLATTENING, BY MEANS OF
VARIABLE THERMAL CONTACT
RESISTANCE

FIG. 5.7

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small a percentage of the overall thermal resistance of the system. As a result, the full variation in thermal conductance due to pressure changes across the interface had only negligible result on the heat input to the thermogenerator analog member. It was decided that the additional effort required to further modify the test setup was not justified due to basic deficiencies of the variable pressure system as compared to other power flattening methods.

Even though the analysis given in section 4.4 and the experimental confirmation of the assumptions made in that analysis indicate that variable pressure power flattening is theoretically feasible it is inferior to other power flattening methods described in this report for the following reasons: weight of the structure required to maintain alignment of the interface, weight of the interface members required from flatness considerations, difficulty of fabricating absolutely leak tight gas enclosure and danger of micrometeorite penetration, difficulty of maintaining uniform flow through the extremely small orifice required, possible extraneous loss through interface at end-of-life. The tendency of mating surfaces to "cold-weld" in space also seriously mitigates against this method.

5.4 Variable Radiator Area Test

A Class II power flattening method incorporating a secondary radiator, the area of which can be varied to obtain regulation of the heat input to the thermogenerator, is described in section 4.5. An experiment was designed and conducted for the purpose of demonstrating this power flattening method.

Figures 5.8 and 5.9 (respectively) are a schematic drawing and a photograph of the apparatus constructed to perform this experiment. A single thermocouple of P and N type lead telluride, and a water-cooled cold junction were used to represent the thermoelectric convertor and the primary radiator. Since the heat input to the thermogenerator and the primary radiator are essentially fixed, it is valid to use water cooling to maintain a constant cold junction temperature.

Electrical heaters in a copper heat spreader were used to represent a radioisotope heat source and variable transformers enabled the heat input to be varied. The thermal

FIG. 5.8

output from the electrical heaters was rejected partly by passing through the thermocouple and partly through two secondary radiators attached to the heat spreader. Thermal insulation was used around the heat spreader and the apparatus was mounted in an evacuated bell jar to eliminate convective heat transfer. A water cooled heat sink was used to receive the heat from the secondary radiators.

The experiment was conducted by introducing a thermal input at time zero, both secondary radiators in place, sufficient to obtain the desired, maximum hot junction temperature. The output power from the thermocouple is then measured. The thermal input is then reduced, analogous to radionuclide decay, until the thermocouple output reaches a minimum acceptable value; at which time a secondary radiator segment is removed from the thermal circuit by means of an electromagnetic actuator.

The output power will then rise and the thermal input is again reduced until the thermocouple output power requires the removal of the second secondary radiator. The reduction in heat input is then continued until the thermocouple output power once again reaches the minimum acceptable value. The thermal input at this point is considered the end-of-life input. The ratio of zero time to end-of-life heat inputs determines the mission time/half-life (θ/h) ratio for the system.

Results

The experiment described above was conducted and the results demonstrate a power-flattened thermoelectric generator, with two radiator segment rejections, which maintains electrical power output within 6% for a mission time/half-life (θ_F/h) ratio of 0.67 as illustrated in Figure 5.10. A hot junction temperature change of $\pm 15^\circ\text{F}$. was required. Table 5.1 presents the results obtained.

Table 5.1

θ/h	Hot Source Temp., °F	Hot Junction Temp., °F	Cold Junction Temp., °F	Radiator Temp., °F	Secondary Radiator Condition
0	705	680	180	495	Both secondary radiators active, start-of-life
.21	675	650	189	480	Reject # 1 radiator
.41	675	650	195	485	Reject # 2 radiator
.67	673	645	185	-	End-of-life

The θ/h ratios in Table 5.1 are determined from actual total heat inputs as measured by a precision wattmeter. If the ratio of heat input at any time to the heat input at start-of-life is known then θ/h can be obtained from the decay relationships.

Figure 5.10 presents a plot of percentage deviation in power output and hot junction temperature versus θ/h . Even though the test was set up in an evacuated chamber, and efforts were made to provide effective thermal insulation of the electrical heat source, large heat losses were found that did not pass through either the single thermoelectric couple or the secondary radiators, losses estimated as 50 % of the total heat input. A well designed thermoelectric convertor using multiple couples would have much smaller losses. Because of these losses some experimental adjustment of the thermal conductance of the heat path from the heat source to the secondary radiators was required. The test was designed so that this adjustment was readily made. If an operating thermoelectric generator were to be made using this method of power flattening, it is expected that some testing using an electrically heated source would be required to obtain an optimum secondary radiator configuration.

The detailed design of a variable area power flattening device would depend upon the overall power source configuration. There are, however, some general problems which have been considered. The radiator rejection may be accomplished by explosive actuators, electro-mechanical actuators, or by springs. If springs are used they should be made of high temperature spring material such as Inconel X or Rene 41.

PERCENT DEVIATION IN POWER
OUTPUT

POWER FLATTENING
VARIABLE AREA RADIATOR

EXPERIMENTAL RESULTS
PERCENT DEVIATION
IN POWER OUTPUT
VS. t/t_h RATIO

T_c COLD JUNCTION
TEMPERATURE = 200F

8
4
0
-4
-8

$T_h = 705F$

1ST RADIATOR

REJECTION

2ND RADIATOR

REJECTION

$T_h = 675F$

END-OF-

LIFE

Pt-N Pt-Te THERMOCOUPLE

MISSION TIME/HALF-LIFE (t/t_h) RATIO

FIG. 5.10

0

2

4

6

8

After a radiator rejection has taken place, it is possible that some areas will be exposed which will be at a high temperature and, therefore, a source of heat loss. It is necessary that this area be minimized and of low emissivity.

Appendix 6.1

NomenclatureDimensions

A	Area (cross-section or surface)	in^2
C	Constant terms as defined in text	-
D	Diameter	ins
E	Electromotive force	volts
F	Free energy	cal/mole
G	Sublimation rate	cms/yr
I	Current	amperes
K	Exponent for polytropic gas process	-
L	Length	ins
M	Molecular weight	-
N	Number of thermocouples	-
P	Electrical power	watts
Q	Heat flow	Btu/hr
Q _C	Conduction heat flow	" "
Q _E	Excess heat not required by convertor	" "
Q _G	Heat flow through convertor	" "
Q _I	Heat flow from radioisotope source	" "
Q _P	Peltier heat absorbed at hot junction	" "
R	Electrical resistance	ohms
R _G	Thermoelectric generator internal resistance	"
R _L	Load resistance	"
S	Entropy	Cal/deg-mole
T	Absolute temperature	°R, °K
T _C	Cold junction temperature	"
T _H	Hot junction temperature	"
T _R	Radiator temperature	"
U	Thermal conductance	Btu/hr-°R
V	Potential difference	volts
W	Sublimation rate	gms/sec-cm ²

X	Constant term used in section 4.5	-
Z	Figure of merit of a thermoelement	$^{\circ}\text{K}^{-1}, ^{\circ}\text{R}^{-1}$
a	Constant used in section 6.8	-
c	Specific heat	Btu/lb- $^{\circ}\text{F}$
h	Half-life of radioisotope	days, yrs.
k	Thermal conductivity	Btu/hr-ft- $^{\circ}\text{F}$
m	Ratio load to internal resistance of a thermoelectric generator	-
p	Gas pressure or vapor pressure	psi, mm Hg.
w	Mass flow rate	lbs/sec
α	Seebeck coefficient	$\mu\text{volts}/^{\circ}\text{C}$
β	Constant used in section 4.6	-
δ	System effectiveness defined in section 3.2	-
δ	Gas constant, section 6.8	ftlbs/lb- $^{\circ}\text{R}$
Δ	Change of	-
ϵ	Emissivity	-
η	Efficiency	-
θ	Time	days, years
θ_F	Mission duration	" "
ρ	Resistivity	$\mu\text{ohm-cms}$
ρ	Boltzman constant	Btu/hr-ft 2 - $^{\circ}\text{R}^4$
ϕ	Function of	-
ψ	Sublimation constant defined in section 4.7	-
ω	Weight in gas in reservoir, section 6.8	lbs.

Subscripts

O	Start-of-life
F	End-of-life
G	Thermoelectric generator
I	Radioisotope source
N _g	Negative thermoelectric element

P Positive thermoelectric element
R Radiator
TE Thermoelectric
u In a sequential power flattening operation, refers to
 time when power output attains a lower acceptable limit.

Superscripts

()' Primed variables pertain to power flattening radiator
 or system
 Unprimed variables refer to primary system

Miscellaneous

TEG Thermoelectric Generator
RTG Radioisotope thermoelectric generator.

Appendix 6.2 References

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Appendix 6.3 Behavior of a RTG System Without Power Flattening.

Sample Calculation of T_{ho} for a Postulated mission following Method Given in Section 3.1:

Given: $T_{hf}, T_{cf}, P, E_{oc}$, material used, and θ_F/h .

Procedure: 1. Determine α, ρ, k for material used, p and n , averaged over temperature range in question.

2a. Calculate figure of merit,

$$Z = \frac{(\alpha_p - \alpha_n)^2}{(\sqrt{k_p \rho_p} + \sqrt{k_n \rho_n})^2}$$

3: Calculate

$$m = \frac{R_L}{R_G} = \sqrt{1 + \frac{1}{2} Z (T_h + T_c)}$$

4. Calculate

$$\eta = \frac{T_h - T_c}{T_h} \cdot \frac{m-1}{m + T_c/T_h}$$

5. $Q_G = P/\eta$

6. $Q_G = Q_c + Q_p$

7. $I = P/V_c$

8. $V_c = \frac{m}{m+1} E_{oc}$

9. $E_{oc} = N \alpha (T_h - T_c)$, solve for N

10. $Q_p = N \alpha I T_h$

11. $Q_c = (k_p A_p + k_n A_n) \frac{N}{L} (T_h - T_c)$

12. $A_p/A_n = \sqrt{\frac{\rho_p k_n}{\rho_n k_p}} = C$

This gives a ratio for A_p/A_n and, if $L_p = L_n$, for $(A/L)_p/(A/L)_n$

13. Combining 12 and 11 gives a solution for $(A/L)_p$ and $(A/L)_n$

14. Select an L so that A_p and A_n can be calculated.

15. The above (2-14) based upon A. F. Ioffe, Semiconductor, Thermoelements and Thermo-electric Cooling Infosearch.
16. Materials properties for lead telluride; P, 0.3 AT % Na; N, 0.03 Mol % PbI₂

Temperature	$\mu\text{V}/^{\circ}\text{R}$ α_n	$\mu\text{V}/^{\circ}\text{R}$ $\alpha_{p,n}$	$\mu\text{V}/^{\circ}\text{R}$ $\alpha_p - \alpha_n$	$\mu\Omega\text{-in}$ ρ_n	$\mu\Omega\text{-in}$ ρ_p	BTU/hr/in ² /^{\circ}\text{R}/in k_n	BTU/hr/in ² /^{\circ}\text{R}/in k_p	Z $^{\circ}\text{R}^{-1}$	$\eta, \%$
1260-830 R	-129	157	286	1090	2480	0.069	0.060	0.0052	4.28

$$17. M = \sqrt{1 + \frac{1}{2} Z (T_h + T_c)} = 1.24$$

$$18. Q_G = \frac{20}{0.0428} = 470 \text{ watts} = 1600 \text{ BTU/hr.}$$

$$19. I = \frac{20}{6} = 3.33 \text{ amperes}$$

$$20. E_{oc} = \frac{(1.24 + 1)}{1.24} 6 = 10.8 \text{ volts}$$

$$21. N = \frac{10.8}{0.000286(1260 - 830)} = 88 \text{ thermocouples}$$

$$22. Q_p = 88 \times 286 \times 3.33 \times 1260 \times 3.41 \times 10^{-6} = 360 \text{ Btu/hr}$$

$$23. Q_c = Q_G - Q_p = 1600 - 360 = 1240 \text{ BTU/hr}$$

$$24. C = \sqrt{\frac{0.248 \times 0.069}{0.060 \times 1090}} = 1.69$$

$$25. Q_c = (k_p A_p + k_n A_n) \left(\frac{N}{L} \right) (T_h - T_c)$$

$$1240 = (0.060 A_p + 0.069 A_n) \left(\frac{88}{L} \right) (430)$$

$$2.89 = (0.101 A_n + 0.069 A_n) \frac{88}{L}$$

Let $L = 0.244$ inches (design choice)

$$17 A_n = (0.244 \times 2.89) / 88$$

$$A_n = 0.047 \text{ in}^2 ; A_p = 0.080 \text{ in}^2$$

26.. Next an evaluation of T_{ho} using the following exact expression from section 3.1.1.

$$\frac{Q_{GF}}{Q_{G0}} = \frac{\left[\frac{N\alpha_F^2 T_{HF}}{R_L + LN\left(\frac{R_{NF}}{A_N} + \frac{R_{PF}}{A_P}\right)} + \frac{K_{PF}A_P + K_{NF}A_N}{L} \right] N(T_{HF} - T_{CF})}{\left[\frac{N\alpha_0^2 T_{ho}}{R_L + LN\left(\frac{R_{N0}}{A_N} + \frac{R_{P0}}{A_P}\right)} + \frac{K_{P0}A_P + K_{N0}A_N}{L} \right] N(T_{ho} - T_{CF}) \sqrt[4]{\frac{Q_{G0}}{Q_{GF}}}}$$

from the decay relationship, with a $\theta_F/h = 0.75$.

$$\frac{Q_{GF}}{Q_{G0}} = 0.6 \quad (\text{See Figure 2.2.1})$$

$$(0.6)^{1/4} = 0.88$$

as a first approximation assume $T_{ho} = 1660$ R
Then the following material properties are assumed

α_0	R_{N0}	R_{P0}	K_{N0}	K_{P0}
248	1350	2240	.067	.059

Substitution of the above values into line 26.
verifies $T_{ho} = 1660$ R

27. If the values given above are substituted into the approximate relationship given in Section 3.2,

$$\frac{Q_{GF}}{Q_{G0}} = \frac{(K_{PF} + K_{NF})(T_{HF} - T_{CF})}{(K_{P0} + K_{N0})(T_{ho} - T_{CF}) \sqrt[4]{Q_{G0}/Q_{GF}}}$$

a value of $T_{ho} = 1675$ R results

28. Additional illustrative cases for a range of values of θ_F/h and T_{ho} were calculated by the method of line 27. The results are shown in Figure 3.4.1

Appendix 6.4 Design of a 20 Watt Thermoelectric Generator

Given: $T_h = 1410 \text{ R}$, $T_c = 830 \text{ R}$,

P type PbTe 0.3 Atom % Na

N type PbTe .03 Mol % PbI_2

$P = 20 \text{ Watts}$, $V_c = 6 \text{ volts}$, $R_L = 1.8 \text{ ohms}$

Average Thermoelectric Properties

Temperature $T_h - T_c$	α_N $\mu\text{V}/^\circ\text{R}$	α_P $\mu\text{V}/^\circ\text{R}$	α_{PN} $\mu\text{V}/^\circ\text{R}$	ρ_N $\mu \text{ cm}$	ρ_P $\mu \text{ cm}$	K_N $\text{BTU/hr/ft}^2/^\circ\text{F/in.}$	K_P $\text{BTU/hr/ft}^2/^\circ\text{F/in.}$	Z $^\circ\text{R}^{-1}$	η %
1410R-830R	-127	146	273	1230	2480	.06	.062	.00047	4.84

1. The Appendix 6.3 procedure will be used
2. $m = \sqrt{1 + \frac{1}{2}(0.00047)(1410 + 830)} = 1.23$
3. $Q_G = 20/.0484 = 414 \text{ Watts} = 1410 \text{ Btu/hr}$
4. $I = 20/6 = 4 \text{ amps}$
5. $E_{oc} = \frac{(1.23 + 1)6}{1.23} = 10.8 \text{ V}$
6. $N = 10.8/(0.000273(1410 - 830)) = 69 \text{ thermocouples}$
7. $Q_P = 69 \times 0.000286 \times 3.33 \times 1410 \times 3.41 = 310 \text{ Btu/hr}$
8. $Q_C = Q_G - Q_P = 1410 - 310 = 1100 \text{ Btu/hr}$
9. $C = A_P/A_N = \sqrt{\frac{2480 \times .060}{.062 \times 1090}} = 1.49$
10. $Q_C = 1100 = (.060 A_P + .062 A_N) \frac{69}{L} (1410 - 830)$
 $= (.09 A_N + .062 A_N) \frac{69}{L} (580)$
Let $L = .244 \text{ ins.}$
Then $A_N = .047 \text{ in}^2$; $A_P = .066 \text{ in}^2$

Appendix 6.5 Class I Power Flattening by Bypass Generator Method

Based on section 4.3 the generator of Appendix 6.4 will be studied to determine the number and nature of changes in the by-pass generator required for a $\theta_F/h = 0.75$.

1. With a $\theta_F/h = 0.75$, the decay relationship dictates that

$$\frac{Q_{I0}}{I_0} = 1.66$$

$$Q_{I0} = 1.66 \times 140 = 2340 \text{ Btu/hr}$$

2. from equation 3.4.6,

$$(1.66)^{1/4} = \frac{T_{co}}{830}$$

$$T_{co} = 940 \text{ R}$$

3. Assume $P_o = 23 \text{ Watts} *$

$$I = \sqrt{P_o/R_L} = \sqrt{23/1.8} = 3.58 \text{ amps}$$

$$Q_c = \frac{N}{L} (K_N A_N + K_P A_P) (T_{ho} - T_{co})$$

$$Q_c = \frac{69}{.244} [.062 \times .044 + .060 \times .066] (T_{ho} - 940)$$

assume that T_{ho} at start of life will not be allowed to exceed 1480R

$$Q_c = 283 \times .00667 \times 540$$

$$Q_c = 1030 \text{ BTU/hour}$$

$$Q_p = N I_o \alpha T_{ho} = 69 \times 3.58 \times .000273 \times 1480$$

$$= 100 \text{ W}_i = 341 \text{ BTU/hour}$$

* A limit on power output of +15% - 10%, 23-18 will be allowed.

4. From the quantity of heat to be passed through the by-pass generator is equal to $2340 - 1030 - 341 = 969$ BTU/hour (eq. 4.3.1)

5. The quantity of heat to be passed through the by-pass generator is also equal to $Q_C' + Q_P'$

$$Q_C' = \dot{Y}(T_{h0} - T_{c0}) = 549 Z' \text{ where } \dot{Y} = \frac{N'}{L}(K_N A_N' + K_P A_P')$$

$$Q_P' = N' \times .000273 \times 3.58 \times 1480 = 1.45 N' \text{ watts} = 4.94 N' \text{ Btu/hr}$$

6. From equation 4.3.4

$$(A/L)' = \frac{969 - 4.94 N'}{33}$$

7. $R_1 = 1.46$ ohms (Appendix 6.4)

$$R_1 + R_L = 3.26 \text{ ohms}$$

From equation 4.3.5

$$E_{oc} = 69 \times .000273 \times (1480 - 940) \\ = 9.86 \text{ volts}$$

$$E'_{oc} = \sqrt{P_o/R_L} (3.26 + R_G') - 9.86$$

$$E'_{oc} = 3.58 R_G' + 1.80$$

$$N' \times (T_{h0} - T_{c0}) = 3.58 R_G' + 1.80$$

$$.148 N' = 3.58 R_G' + 1.80$$

8. $A_N = .67 A_P$ (Appendix 6.4)

$$C = .67$$

9. From equation 4.3.6 and line 6 of this Appendix

$$R_G' = \left[\rho_P (1+C) + \frac{1+C}{C} \rho_N \right] \frac{N'^2}{(A/L)'} \\ = \left[.00415 + .00308 \right] \frac{N'^2 \times 33}{969 - 4.94 N'} = \frac{.24 N'^2}{969 - 4.94 N'}$$

10. From lines 7 and 9

$$.148 N' = \frac{3.58 \times (.24 N')^2}{969 - 4.94 N'} + 1.80$$

$$\text{or } N' = 13$$

11. From lines 6, 9 and 10, $(A/L)' = .29$ in, $R_G' = 0.042$ ohms

12. From equation 4.3.8

$$P_u = \frac{(N + N') (T_{hu} - T_{cu})^2 R_L}{(R_G + R_G' + R_L)^2}$$

$$\text{Let } P_u = 18 \text{ watts, } R_G + R_G' + R_L = 3.30$$

$$\text{Then } (T_{hu} - T_{cu}) = 467^\circ \text{R}$$

13. From equation 4.3.9

$$Q_{Iu} = (1.89 + 1.77)(467) + (69 + 13)(.000273) I T_{hu} (3.41) \\ = 1710 + .076 I T_{hu}$$

$$I = \sqrt{18/1.8} = 3.17$$

$$T_{hu} = T_{cu} + 467$$

$$Q_{Iu} = 1410 (T_{cu}^4 / 830^4)$$

$$\frac{1410 \left(\frac{T_{cu}}{100} \right)^4}{(8.30)^4} = 1710 + .24 (T_{cu} + 467)$$

Then $T_{cu} = 900 \text{ R}$

$$Q_{Iu} = 1410 (1.387) = 1960 \text{ Btu/hr}$$

(from the decay relationship).

14. From equation 4.3.11

$$3.58 = \frac{.000273(69 + N'_u)(T_{hu} - 900)N'_u}{3.26 + \left[\frac{q_p}{(A/L)_p} + \frac{q_u}{(A/L)_u} \right]}$$

for by-pass generator.

$$(A/L)_p = 1.49 (A/L)_n \text{ (Appendix B)}$$

$$(A/L)_{\text{thermocouple}} = 2.49 (A/L)_n$$

$$(A/L)_{\text{thermocouple}} = 29/13 = 2.23$$

$$(A/L)'_n = .897$$

$$(A/L)'_p = 1.34$$

Thus,

$$28.6 + .258 N'_u = .0188 T_{hu} + .000273 N'_u T_{hu}$$

15. From equation 4.3.12

$$1960 = .061 [31 + (.897 + 1.34) N'_u] (T_{hu} - 900) + (69 + N'_u) (.00273) 3.58 T_{hu}$$

From line 14 of this Appendix

$$T_{hu} = \frac{28.6 + .258 N'_u}{.0188 + .000273 N'_u}$$

$$\text{Thus, } N'_u = 2 \text{ couples}$$

$$T_{hu} = 1510 \text{ R}$$

16. Since the T_{hu} of 1510 R just calculated is over the 1480 R limit, the equation from line 14,

$$T_{hu} = \frac{28.6 + .258 N'_u}{.0188 + .00273 N'_u} \quad \text{must be solved for } T_{hu} = 1480 \text{ R} \\ \text{giving}$$

$$N'_u = 4 \text{ couples}$$

17. The next step is to determine the time of the next change.

18. From equation 4.3.8

$$18 = \frac{[(69+4)(.000273)(T_{hu}-T_{cu})]^2 (1.8)}{(3.26 + R'_G)^2}$$

$$\text{or } R'_G = .0129 \Omega$$

$$T_{hu} - T_{cu} = 520 \text{ F}$$

From equation 4.3.9

$$Q_{Iu} = (1.89 + .543)(520) + (73)(.000273)(3.17)(3.91) T_{hu} \\ = 1260 + .21(T_{cu} + 520) = 1410 \quad T_{cu} \neq 830^+$$

$$\text{Thus, } T_{cu} = 837 \text{ R}$$

$$Q_{Iu} = 1460 \text{ Btu/hr}$$

$$\theta/h = 0.7$$

Remove last 4 thermocouples.

Appendix 6.6 Class II Power Flattening by Variable Thermal Conductivity Method

If a member whose thermal conductivity varies inversely with temperature is placed between the heat source and the thermoelectric generator and if a member whose thermal conductivity varies directly with temperature is placed between the heat source and the secondary radiator, it is possible to achieve effective power flattening as discussed in 4.8. The purpose of this Appendix is to develop numerical results for a specific problem as illustrated in Figure 4.8.1.

It is apparent from equation 4.8.2 that materials are needed for the temperature sensitive members having the largest possible change in thermal conductivity over the temperature range of interest. The best materials found were beryllia between the source and the convertor and Fiberfrax* between the heat source and the secondary radiator. Figures 6.6.1 and 6.6.2 give data for thermal conductivity versus temperature for beryllia and Fiberfrax.

From equation 4.8.1

$$1. \quad \frac{T_{R_0}^4}{T_{R_F}^4} = \frac{K_{I_0} (T_{I_0} - T_{R_0})}{K_{I_F} (T_{I_F} - T_{R_F})}$$

From Figure 6.6.2 the following relationships can be derived:

$$2. \quad K_{I_0} = \frac{\frac{1}{2} (T_{I_0} + T_{R_0}) - 610}{888}$$

$$3. \quad K_{I_F} = \frac{\frac{1}{2} (T_{I_F} + T_{R_F}) - 610}{888}$$

Combining lines 1, 2 and 3 gives

$$4. \quad \frac{T_{R_0}^4}{T_{R_F}^4} = \frac{T_{I_0} - T_{R_0}}{T_{I_F} - T_{R_F}} \cdot \frac{\frac{1}{2} (T_{I_0} + T_{R_0}) - 610}{\frac{1}{2} (T_{I_F} + T_{R_F}) - 610}$$

* Trade name, Carborundum Co.

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FIG. 6.6.2
THERMAL CONDUCTIVITY
OF FIBERFRAX
^{1/5}
TEMPERATURE

THERMAL CONDUCTIVITY BTU-IN
/HR-FT²-°F

1.5
1.4
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
0

0 700 900 1100 1300 1500

TEMPERATURE, °F

Case I

$$T_{I_0} = 2460 R$$

$$T_{IF} = 1760 R$$

$$T_{RF} = 960 R$$

$$Q_G = 1400 \text{ Btu/hr}$$

$$\theta_F/h = 0.75$$

Line 4 gives

$$\frac{T_{R_0}^4}{960^4} = \frac{2460 - T_{R_0}}{1760 - 960} \cdot \frac{\frac{1}{2}(2460 + T_{R_0}) - 610}{\frac{1}{2}(1760 + 960) - 610}$$

$$\text{or } T_{R_0} = 1200 R$$

From equation 4.8.1

$$\frac{Q_{E0}}{Q_{EF}} = \left(\frac{1200}{960} \right)^4 = 2.47$$

From above results and the exponential decay law,

$$Q_{IF} = Q_G + Q_{EF} \quad \text{at } \theta = \theta_F$$

$$1.66 Q_{IF} = 1400 + 2.47 Q_{EF} \quad \text{at } \theta = 0$$

$$Q_{EF} = 1150 \text{ Btu/hr}$$

Case II

$$T_{I_0} = 2460 R$$

$$T_{IF} = 1660 R$$

$$T_{RF} = 960 R$$

$$\frac{T_{R0}^4}{960^4} = \frac{2460 - T_{R0}}{1660 - 960} \cdot \frac{\frac{1}{2}(2460 + T_{R0}) - 610}{\frac{1}{2}(1660 + 960) - 610}$$

$$T_{R0} = 1270 R$$

$$\frac{Q_{E0}}{Q_{EF}} = \left(\frac{1270}{960} \right)^4 = 3.06$$

$$\therefore Q_{EF} = 271 \text{ Btu/hr}$$

Since this is not an unreasonable value of Q_{EF} , it is now possible to examine the actual fluctuation in Q_G

From equation 4.8.2

$$\frac{Q_{G0}}{Q_{GF}} = \frac{K_{20} \cancel{(A/L)}_2 (T_{I0} - T_h)}{K_{2F} \cancel{(A/L)}_2 (T_{IF} - T_h)}$$

The following expression for the thermal conductivity of high density beryllia can be derived from Figure 6.6.1:

$$K_{2p} = \frac{232}{\left(\frac{5}{9} \bar{T} \right)^{.97} - 130}$$

where $\bar{T}$ = mean temperature, °R

Combining the above yields,

$$\frac{Q_{G0}}{Q_{GF}} = \frac{\frac{T_{I0} - T_h}{\left[\frac{5}{9} (\frac{T_{I0} + T_h}{2}) \right]^{.97} - 130}}{\frac{T_{IF} - T_h}{\left[\frac{5}{9} (\frac{T_{IF} + T_h}{2}) \right]^{.97} - 130}}$$

$$\frac{Q_{G0}}{Q_{GF}} = \frac{\frac{(2460 - T_h)}{\left[\frac{5}{9} \left(\frac{2460 + T_h}{2} \right) \right]^{.97} - 130}}{\frac{(1660 - T_h)}{\left[\frac{5}{9} \left(\frac{1660 + T_h}{2} \right) \right]^{.97} - 130}}$$

if, $T_h = 1400 R$

$$Q_{G0}/Q_{GF} = 3.28$$

if, $T_h = 1160 R$

$$Q_{G0}/Q_{GF} = 1.7$$

if, $T_h = 960 R$

$$Q_{G0}/Q_{GF} = 1.44$$

It is thus apparent that T_h must approach an unattainable low value before Q_{G0}/Q_{GF} will approach unity.

Appendix 6.7 Class II Power Flattening by Variable Radiator Area Method.

Calculation of variable area radiator power flattening system for the end-of-life generator described in Appendix 6.4 and a $\theta_F/h = 0.75$

Given: $Q_G = 414 \text{ Watts} = 1410 \text{ Btu/hr} = Q_{IF}$

$$\theta_F/h = .75$$

$$T_{I_0} = 1800 \text{ R}$$

$$T_{R_0} = 1200 \text{ R}$$

$$\epsilon = .75$$

1. From the discussion in section 4.5 tolerances on Q_G and T_I are assigned. This results in

$$Q_G' = 1300, \quad Q_G'' = 1525, \quad T_I' = 1650 \text{ R}, \quad T_I'' = 1950 \text{ R}$$

$$Q_{G_0} = Q_G''$$

$$T_{I_0} = T_I''$$

2. From the decay relationship and since $Q_E = Q_I - Q_G$

$$Q_{I_0} = 1.66 Q_G = 2320 \text{ Btu/hr}$$

$$\begin{aligned} Q_{E_0} &= Q_{I_0} - Q_G \\ &= 2320 - 1448 = 872 \text{ Btu/hr} \end{aligned}$$

3. From equation 4.5.1

$$A_R' = \frac{872}{.174 \times .75 \times \left(\frac{1200}{100}\right)^4} = .319 \text{ ft}^2$$

4. From equation 4.5.2

$$U_{E_0} = \frac{872}{1950 - 1200} = 1.16 \text{ Btu/hr-}^\circ\text{F}$$

5. From equation 4.5.4

$$Q_{I1} - 1300 = 1.16 \left[1650 - 100 \sqrt[4]{\frac{Q_{I1} - 1300}{.174 \times .75 \times .319}} \right]$$

$$Q_{I1} = 1960 \text{ Btu/hr}$$

6. Thus, $\theta_1/h = .24$

7. From equation 4.5.5

$$1960 - 1525 = 1.16 \left[1950 - 100 \sqrt[4]{\frac{1960 - 1525}{.174 \times .75 \times .319 X}} \right] X$$

whence $X = 0.5$, new $U_E = 0.58$, new $A'_R = .159$

8. Repeat step 4 with new A'_R and new U_E

$$Q_{I2} - 1300 = .58 \left[1650 - 100 \sqrt[4]{\frac{Q_{I2} - 1300}{.174 \times .75 \times .159}} \right]$$

whence, $Q_{I2} = 1620 \text{ BTU/hour}$

$$\theta_2/h = .52$$

9. Repeat step 6 with new values of Q_{I2}

$$1650 - 1525 = 1.16 \left[1950 - 100 \sqrt[4]{\frac{1620 - 1525}{.174 \times .75 \times .319 X}} \right] X$$

$X = 0.11$, new $U_E = .128$, new $A'_R = .035 \text{ ft}^2$

10. Repeat step 4 using new U_E and new A'_R

$$Q_{I3} - 1300 = .128 \left[1650 - 100 \sqrt[4]{\frac{Q_{I3} - 1300}{.174 \times .75 \times .035}} \right]$$

whence $Q_{I_3} = 1370$ BTU/hour

Therefore, it is not necessary to remove the balance of the radiator area until the end-of-life so that in actuality it need not be removed at all!

Appendix 6.8 Pressure versus Time for a Gas Leaking Thru an Orifice

The purpose of this appendix is to derive an expression for pressure versus time for the variable pressure power flattening system described in section 4.4 of this report. In this system gas escapes from a bellows through a small orifice. It is assumed that:

1. Gas escapes from the orifice adiabatically and without friction.
2. The temperature of the gas in the container is constant.
3. The gas escapes to space at 0 psia.

Mark's Mechanical Engineers Handbook, 5th edition, page 333 gives the following expression for critical, isentropic flow

$$1. \quad \omega = C A_o P \sqrt{\frac{g}{\delta T_i} K \left(\frac{2}{K+1} \right)^{(K+1)/(K-1)}}$$

From the perfect gas law,

$$2. \quad p = \frac{\delta T}{V} \omega \quad \text{where } \delta, \omega, \text{ and } V \text{ are constant}$$

$$3. \quad \text{at any time } t, \quad \frac{dp}{dt} = \frac{\delta T}{V} \frac{d\omega}{dt}$$

At any time t , during a small interval of time dt , the change in mass in the bellows must equal the flow out of the orifice. Therefore, $d\omega = -\omega dt$, where the negative sign is used to show that a decrease in mass occurs.

Therefore,

$$4. \quad \frac{dp}{dt} = \frac{\delta T}{V} \left(\frac{-\omega dt}{dt} \right) = - \frac{\delta T \omega}{V}$$

Combining lines 2 and 4 gives

$$5. \quad \frac{dp}{p} = -\frac{\delta T}{V} CA_0 \sqrt{\frac{g}{\delta T_1}} K \left(\frac{2}{K+1} \right)^{(K+1)/(K-1)} dt$$

$$6. \quad \int \frac{dp}{p} = -\frac{\delta T}{V} CA_0 \sqrt{\frac{g}{\delta T_1}} K \left(\frac{2}{K+1} \right)^{(K+1)/(K-1)} \int dt$$

$$7. \text{ For simplicity let, } a = \frac{\delta T_1}{V} CA_0 \sqrt{\frac{g}{\delta T_1}} K \left(\frac{2}{K+1} \right)^{(K+1)/(K-1)}$$

$\therefore \ln p = -at + E$, where E is a constant of integration.

Solving for E when $t = 0$, $p = p_0$, $\ln p_0 = E$ gives

$$7. \quad \ln p - \ln p_0 = at$$

$$\text{or } p = p_0 e^{-at}$$

Thus, a gas leaking thru an orifice as described gives an exponential variation in pressure in the reservoir.

Appendix 6.9 Rates of Dissociation and Evaporation of Inorganic Compounds

Reference: Dushman, pg. 797 ff. [13]

Derivation:

Consider the following generic reaction between a metal M and a non-metal N, both in gaseous form at some elevated temperature T,

where (s) and (g) denote solid and gaseous phases, respectively. The free energy increase per gram mole of $M_m N_n$ is ΔF_i .

Let ΔF_o denote the increase in free energy of the reaction,

and let ΔF_r be the increase in free energy of the reaction,

Then $\Delta F_i = \Delta F_o + \Delta F_r$. If the reaction is carried out in a volume at temperature T,

$$\Delta F_i = R_o T \ln K_1 \quad \dots 6.9.4$$

where $K_1 = P_{atm}(M)^m \cdot P_{atm}(N)^n \quad \dots 6.9.5$

Also, $\Delta F_r = R_o T \ln P'_{atm}(M) \quad \dots 6.9.6$

Substituting, $P_{atm}(M) = \frac{m}{n} P_{atm}(N)$ into 6.9.5 we obtain

$$\ln K_1 = m \ln P_{atm}(M) + n \ln P_{atm}(M) + n \ln \frac{n}{m} = \frac{\Delta F_i}{R_o T} \quad \dots 6.9.7$$

Substituting 6.9.6 into 6.9.7 and solving for $\ln P'_{atm}(M)$ we obtain

$$\ln P'_{atm}(M) = \frac{\Delta F_o}{R_o T(m+n)} + \frac{\ln P_{atm}(M)}{(m+n)} - \frac{n \ln \frac{n}{m}}{(m+n)} \quad \dots 6.9.8$$

Converting to pressures in millimeters of mercury ($\log_{10} 760 = 2.881$) and to logarithms in the base 10 ($\ln N = 2.303 \log N$) we obtain,

$$\log P(M) = \frac{\Delta F_0}{R_0 T(m+n)(2.303)} + \frac{\log P'_{-2.881}}{(m+n)} - \frac{n \log \frac{n}{m}}{(m+n)} + 2.881 \dots 6.9.9$$

With $R_0 = 1.986 \text{ cal/}^\circ\text{C per mole}$, 6.9.9 simplifies to

$$\log P(M) = \frac{\Delta F_0/T}{4.574(m+n)} + \frac{\log P'}{(m+n)} - \frac{n \log \frac{n}{m} + 2.881}{(m+n)} + 2.881 \dots 6.9.10$$

where $P'(M)$ = vapor pressure of M over solid or liquid M in mm. Hg.

$P(M)$ = vapor pressure of M over compound $M_m N_n$ (= dissociation pressure) in mm.Hg.

For the case of a compound such as cupric oxide (CuO): $m=1$, $n=1/2$ so that 6.9.10 becomes

$$\log P(\text{Cu}) = \frac{\Delta F_0/T}{6.861} + \frac{2}{3} \log P' + 1.061 \quad 6.9.11$$

1. Sample Calculation for Dissociation of Cupric Oxide at 1000°K.

From Dushman pg. 806, $\Delta F_0/T = -16.55 \text{ at } 1000 \text{ K}$

From WADC-TR58-476, $P' = 9 \times 10^{-8} \text{ mm Hg}$

$$\log P = -\frac{16.55}{6.861} + \frac{2}{3}(23.954 - 30) + 1.061 = -$$

$$P = 2.3 \times 10^{-5} \text{ mm Hg}$$

The rate of evaporation is given by the Langmuir equation,

$$G_{\text{CuO}} = 1.86 \times 10^6 \frac{P}{P_{\text{CuO}}} \left(\frac{M_{\text{Cu}}}{T} \right)^{1/2}$$

$$= \frac{1.86 \times 10^6 \times 2.3 \times 10^{-5}}{6.40} \left(\frac{63.57}{1000} \right)^{1/2} = 1.69 \text{ cms/yr.}$$

By comparison the rate of evaporation of pure copper is

$$G_{Cu} = \frac{1.86 \times 10^6 \times 9 \times 10^{-7}}{8.92} \left(\frac{63.57}{1000} \right)^{1/2} = 4.74 \times 10^{-2} \text{ cms/yr}$$

2. Dissociation of Cupric Oxide at 900°K

In a similar manner, $\Delta F_0/T = -20.46$

$$P' \doteq 2 \times 10^{-9}$$

$$\log P = -\frac{20.46}{6.861} + \frac{2}{3}(21.301 - 30) + 1.061 = -7.73$$

$$P = 5.3 \times 10^{-7}$$

$$G_{CuO} = \frac{1.86 \times 10^6 \times 5.3 \times 10^{-7}}{6.40} \left(\frac{63.57}{900} \right)^{1/2} = 4.1 \times 10^{-2} \text{ cms/yr}$$

Thus, a decrease of 100°K (from 1000 to 900) results in a rate of evaporation lower by two orders of magnitude. This will be typical of the behavior of simple inorganic compounds such as oxides and sulfides because of the dominating role played by the vapor pressure P' , and the fact that the rates of change of vapor pressure with temperature are similar for all metals of interest in power flattening.

3. Dissociation of Barium Oxide at 1000°K

As a final illustration, let us consider the dissociation of the oxide of a "volatile" metal. For barium oxide at 1000°K, Lewis and Randall give $\Delta F_0/T = -23.00$. The vapor pressure P' is 9×10^{-2} . Therefore,

$$\log P = -\frac{23.00}{6.861} + \frac{2}{3}(28.954 - 30) + 1.061 = -2.99$$

$$P = 9.8 \times 10^{-2} \text{ mm Hg}$$

$$G_{BaO} = \frac{1.86 \times 10^6 \times 9.8 \times 10^{-2}}{5.72} \left(\frac{137.3}{1000} \right)^{1/2} = 1.18 \times 10^4 \text{ cms/yr}$$

In this case there is comparatively little difference between the rates of evaporation of barium over the

pure metal versus barium over barium oxide.

The rates of evaporation of various inorganic compounds of interest in power flattening are shown in Table 4.6.4.

Appendix 6.10 Derivation and Discussion of the Langmuir Equation

Reference: E. H. Kennard, Kinetic Theory of Gases, McGraw-Hill, N. Y. (1938)

If one imagines a small plane surface of area S drawn anywhere in a uniform gas having no mass motion, molecules will be continually crossing S in both directions. By assuming a Maxwellian velocity distribution, it is relatively easy to obtain the total number of molecules crossing S in one direction.

$$\Gamma = \frac{1}{4} n \bar{V} \quad \dots 6.10.1$$

where n = no. of molecules per unit volume
 $\bar{V}$ = mean molecular speed

Substituting the perfect gas law relations in 6.10.1 we obtain for the mass rate of flow

$$\Gamma = \frac{p M^{1/2}}{(2\pi R_0 T)^{1/2}} \quad \dots 6.10.2$$

where R_0 = universal gas constant per mole
 M = molecular weight of gaseous species
 T = absolute temperature
 p = pressure

Equation 6.10.2 is directly applicable to the case of evaporation from a substance in the solid or liquid states. Briefly, consider the equilibrium between evaporation and condensation processes at the free surface of a heated solid. Observe that the maximum rate of evaporation is attained if the vapor is removed as fast as it is formed, so that there is no condensation. Also, since when the vapor is saturated, evaporation equals condensation, the maximum rate of evaporation equals the rate of condensation when the vapor is saturated. This latter quantity is calculated by assuming that a factor α represents the fraction of the total number of molecules impinging on a surface that actually condense. Thus, $W = \Gamma \alpha$ or

$$W = \alpha \frac{p M^{1/2}}{(2\pi R_0 T)^{1/2}} = \frac{\alpha p}{17.14} \left(\frac{M}{T}\right)^{1/2} \quad \dots 6.10.3$$

where the symbols are defined in section 4.6.3.

Finally, if we divide 6.10.3 by the density ρ and convert to the proper dimensions we obtain

$$S = 1.85 \times 10^6 \frac{\alpha p}{\rho} \left(\frac{M}{T} \right)^{1/2} \quad \dots 6.10.4$$

where S is the rate of evaporation in cms/yr.

The coefficient α is known by several names - evaporation coefficient, accommodation coefficient or sticking coefficient. Experimental measurements on a large variety of materials has shown that α is equal to unity ($= 1$) for most metals and for many non-metals such as graphite. For inorganic non-metals the value of α can be appreciably less than unity but this is attributed to the breakdown of the Langmuir equation. This no longer applies because of dissociation or decomposition of the compound and the attendant ambiguity of the various terms in the Langmuir equation.

From the foregoing we conclude that 6.10.3 represents the rate of evaporation into a high vacuum; i.e., in the case of a surface evaporating in space the equilibrium process used to derive the Langmuir equation becomes applicable even though the actual process is non-equilibrium. The major complicating factor is this: if some of the evaporating molecules are not removed from the vicinity of the free surface (i.e., removed an order of distance of several mean free paths) then a vapor cloud develops.

The rate of evaporation is thereby reduced to

$$W = \alpha (p - p_a) / (2 \pi R_0 T)^{1/2} \quad \dots 6.10.5$$

where p_a = pressure of the vapor cloud.

It is assumed in 6.10.5 that the pressure p_a is so low that no diffusional resistance is presented to the evaporating molecules.

In the discussion and analysis of the power flattening methods of section 4.6 and 4.7 we have simplified the picture by assuming $\alpha = 1$ and $p_a = 0$. This assumption would yield a conservative design since the actual evaporation rates would be lower than the calculated values so that the thermocouples would tend to run below design temperature rather than above.

Appendix 6.11 Calculation of Free Energy Change

In order to obtain the dissociation pressure of an inorganic compound by use of equation 6.9.11 we require the free energy change ΔF_T° for the reaction

The value of ΔF_T° must be obtained at the reaction temperature T. Since

$$\Delta F_T^\circ = \Delta F_{M_m N_n}^\circ - n \Delta F_N^\circ - m \Delta F_M^\circ$$

where $\Delta F_N^\circ = \Delta F_M^\circ = 0$ if M, N are elemental substances

$$\Delta F_T^\circ = \Delta F_{M_m N_n}^\circ$$

Therefore the value sought is actually the heat of formation of the compound. Values of the standard heat of formation of many compounds at 298°K are given in Lange [25]. To obtain the value at temperature T, we may use the data on heat content and entropy given by Kelley [17]:

$$\Delta F_T^\circ = \Delta F_{298}^\circ + \Delta(H - H_{298})$$

Additional sources of data in more convenient form are given by and Randall [18] and Dushman [13] where ΔF_T° is given for a large number of simple compounds for a range of temperatures. In this program we have used the most convenient methods provided by the available sources. However, since the data given by Lange and Kelley is most comprehensive a sample calculation of ΔF_T° for copper oxide is given below in order to show the method.

Sample Calculation of ΔF_T° for CuO at 1000°K

From Lange: $\Delta F_{298}^\circ = -30400 \text{ cal/mole}; S_{298} = 10.4$

From Kelley: $H_{1000} - H_{298} = 8680$
 $S_{1000} - S_{298} = 14.58$ } for CuO(s)

$$\therefore S_{1000} = 14.58 + 10.4 = 24.98$$

$$(TS)_{298} = 298 \times 10.4 = 3100$$

$$(TS)_{1000} = 1000 \times 24.98 = 24980$$

$$\Delta F_{1000}^{\circ} = \Delta F_{298}^{\circ} - (H_{1000} - H_{298}) + (TS_{1000} - TS_{298})$$

$$\frac{\Delta F_{1000}^{\circ}}{T} = (-30400 - 8680 + 24980 - 3100) \div 1000 = -17.20$$

This compares closely with the value given by Dushman equal to -16.55 which was probably computed from earlier, slightly different, thermodynamic data.

Appendix 6.12 Some Other Methods for Obtaining Power Flattening By Use of Evaporating Materials

In sections 4.6 and 4.7 we have discussed the evaporation and decomposition of pure metals, metal oxides and metal sulfides as possible ways to utilize evaporation into space for power flattening. A number of other interesting possibilities were not quantitatively evaluated because of time limitations but will be briefly mentioned here for the sake of completeness.

1. Some potentially interesting decomposition reactions involve the reduction of stable oxides in the presence of other metals. For example,

2. The decomposition of certain nitrides seems to be in the proper range of values of pressure and temperature. For example, for a decomposition pressure of 1×10^{-3} mm Hg. the following temperatures apply to the respective compounds:

Ba_3N_2		794°C
CrN		533
Li_3N_2		727
Mn_3N_2		282-915

There is a great deal of uncertainty attached to all of the above values because of experimental difficulties in obtaining accurate data of this type.

3. If operation at radiator temperatures below 1400°F are considered a number of other possibilities arise. For example, the rate of evaporation of magnesium-lithium-aluminum alloys at 800°F is in a suitable range. For LA141 alloy the rate is .88 cm/yr. and for LA91 alloy the rate is .26 cm/yr. Not enough thermodynamic data is available to enable accurate extrapolation to higher temperatures. The melting point of these alloys is about 1200°F. and we estimate that the maximum useful temperature for power flattening is about 1000°F. In this range they would be suitable for application in the variable base area method.

4. The effect of space environment on oxides is unknown at present. According to present knowledge, above 14000 miles altitude the atmosphere consists of 85% atomic hydrogen ions H^+ and 15% helium ions He^{++} . It is conceivable that above 1000 miles there will be sufficient activity of hydrogen to reduce any oxides to the metallic elements, the rate depending on the type of oxide and the operating temperature. Further investigation of this question is necessary. (Below 500 miles altitude this process is not believed to be of serious importance).
5. Diffusion of metals through oxide films will gradually lower the emissivity of an oxide-sprayed or anodized surface in space environment. The porosity and structure of the metal oxide play a major role in governing the rate of diffusion. The reverse process has been found to occur in titanium oxide, where the oxygen gradually diffuses through the titanium and disappears from the surface. This would also lead to a gradual decrease in emissivity with time.
6. The Air Force is presently studying several materials for use as dry lubricants at temperatures above 1000°F. We estimate that the emissivity of some of these would be quite high (perhaps approaching 0.9) and that the rates of evaporation might be reduced by the dilution of the binders. Potentially interesting materials for variable emissivity surfaces are:
 - a. PbO + silicate and borate binders
 - b. PbS + borate binders
7. Two general rules which apply to the selection of compounds for evaporative power flattening may be stated:
 - a. All compounds formed with the evolution of heat tend to decompose when the temperature is raised.
 - b. Low ambient pressure tends to increase the tendency to dissociate when the reaction results in an increase in the number of molecules as when one molecule of a carbonate decomposes to two or three molecules (metal, Oxygen and carbon monoxide).

To illustrate, the heats of formation of some carbonates may be tabulated alongside the approximate temperatures of dissociation into the oxides. There is a clear correlation

between the heat evolved and the temperature, although this data alone is not sufficient to indicate the rates of reaction.

Carbonate of	Heat of formation from oxide, cal.	Temperature* of Dissociation °C
Silver	20,100	225
Lead	22,600	302
Manganese	23,500	330
Calcium	42,500	900
Strontium	55,800	1150

* Reference 26.