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MEMORANDUM #9

EFFECTS OF SUBLIMATION ON SILICON-GERMANIUM RTG PERFORMANCE

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INTRODUCTION

In the operation of a Radioisotope Thermoelectric Generator (RTG) it is usual to focus attention on the electrical performance of the generator as a function of operating time. Although this attention is commonly directed towards the electrical contacts and basic diffusion related phenomena occurring in the thermoelements, it is frequently also necessary to consider other processes, such as vapor phase transport and compatibility of materials used in generator construction. An example of the latter processes is the sublimation commonly experienced with lead telluride and related thermoelectric materials in operation at elevated temperatures. Although sublimation has never proven of consequence in the operation of silicon-germanium RTG's at temperatures commonly used in the past, of the order of 1000°C and less at thermoelement hot junctions, the projected use of still higher temperatures has recently brought the question of sublimation to the fore even for RTG's of this type. Specifically, the Multi-Hundred Watt (MHW) RTG is being designed for beginning of life operation at a nominal thermoelement hot junction temperature of 1100°C; the single stage and cascaded MHW RTG's are both designed for this same beginning of life hot junction temperature. In view of the fact that one proposed use of the MHW RTG requires its useful operation for ten years or longer, the use of it in the Grand Tour mission as a power source for on-board spacecraft power, it is of importance to consider the question of silicon-germanium thermoelement sublimation in terms of its operating temperature and time and to uncover problems, if any, that may be related to the high beginning of life operating temperatures.

Although independent investigations *, both analytical as well as experimental, are presently being conducted on a variety of thermodynamic and kinetic processes that may contribute to the sublimination of silicon-germanium alloys as a result of interactions between these alloys and other materials

* Those conducted at Resalab and at Gulf General Atomics.

commonly used in RTG construction, such as various thermal insulations, the intent of the present study is to use published data on the vapor pressures of silicon and germanium and to calculate the effects of sublimation on typical silicon-germanium thermocouple performance by assuming a simple sublimation model. In order to give the study a measure of practicality, use has been made, although in a simplified form, of the basic thermocouple configuration proposed for use in the single stage MHW RTG.

SUBLIMATION RATE OF SILICON-GERMANIUM ALLOYS

Inasmuch as very few quantitative experimental data on the sublimation of silicon-germanium alloys have ever been reported, it is most expeditious to use the vapor pressures of silicon and germanium in order to estimate the sublimation rates of silicon-germanium alloys. For this purpose, in the present study use will be made of the commonly used vapor pressure data for silicon and germanium reported by Honig. Using these data it is possible to calculate the rate of sublimation, m, of silicon and germanium as a function of temperature by means of the well known relationship

$$m = \left[\frac{M}{2\pi RT}\right]^{1/2} p$$

where M is the atomic weight of the material, R is the universal gas constant, T is the absolute temperature and p is the vapor pressure at temperature T. It should be noted that the sublimation rates calculated by means of the given relationship pertain to free sublimation in which the sublimed species is removed immediately after its formation; no inhibition of sublimation due to surrounding vapor that exists to various degrees in most actual situations is taken into account by the relationship. The relationship thus yields the upper limiting sublimation rate of a given material.

Whereas the sublimation rates of silicon and germanium can therefore be conveniently calculated from published data on vapor pressures of these materials it is not possible to accurately do that for alloys of silicon and germanium. The sublimation rates used for silicon-germanium alloys, in the present study specifically the 80 a/o Si - 20 a/o Ge alloy designated for the MHW RTG, are therefore interpolations between the calculated sublimation rates of silicon and germanium. It is realized that this procedure represents an over simplification because in essence it assumes independence of silicon and germanium sublimation from the alloy. In actual fact it is probably the sublimation rate of the element with the lower sublimation rate, silicon, that represents the equilibrium sublimation rate of the alloy; the higher vapor pressure component, germanium, preferentially tends to sublime from the surface of the alloy, thereby leaving a silicon-rich surface layer. Further sublimation of germanium is preceded by diffusion to the surface, a relatively slow process. Because commonly used silicon-germanium alloys are polycrystalline materials with great concentrations of imperfections and grain boundaries, it is, however, not possible to use bulk diffusion rates in order to definitely establish the validity of this assumption. This same reservation applies to any questions relating to the diffusion and sublimation of dopants used in silicon-germanium alloys. It has therefore been decided in the present instance to obtain sublimation rate data for silicon-germanium alloys by interpolation between the data calculated for silicon and germanium. The latter data are shown in Figure 1 as a function of temperature. For comparative purposes, Figure 1 also includes sublimation rates of some other commonly used thermoelectric materials, namely those of TAGS and of lead telluride. Moreover, the few quantitative experimental data ever obtained on the sublimation of silicon-germanium alloys are also shown in Figure 1. It is noted that of the two sets of experimental data, it is those obtained at Sandia Laboratories that fall in between the calculated sublimation rates of silicon and germanium and thereby reasonably agree with sublimation rates obtained for silicon-germanium alloys by means of interpolation. It is not known why the other experimental data indicate substantially higher sublimation rates.

EFFECTS OF SUBLIMATION ON SiGe THERMOCOUPLE PERFORMANCE

A relatively simple model has been assumed in the present investigation of the effects of sublimation on silicon-germanium Air-Vac thermocouple performance. In order to give the study immediacy, all analyses have been conducted on the thermocouple configuration designated for use in the single-stage foil insulated MHW RTG. For analytical convenience it has been assumed that the n- and p-type thermoelements of the couple both possess circular cross-sections, that the sublimation rates of both types of silicon-germanium are identical and that sublimation from each thermoelement is unimpeded by the proximity of the other. Although these simplifications are strictly non-rigorous, it is believed that they are satisfactory for the present purposes of determining gross sublimation effects on silicon-germanium thermocouple performance. It should be pointed out that although it has been assumed that the thermoelements possess circular cross-sections, the areas of each thermoelement have been maintained at their MHW RTG design values. The assumption of independence of sublimation of each thermoelement has been experimentally found to be not true, but does enable considerable analytical simplicity. In actual fact, sublimation from the sides of the thermoelements facing each other is reduced because of a baffling effect. The present investigation only concerns itself with sublimation of the silicon-germanium thermoelements; effects due to sublimation of the silicon-molybdenum hot shoe are thus not taken into account. Although it has been experimentally found that considerable sublimation of the hot shoe material occurs at elevated operating temperatures, it is possible to minimize the effects of this through the use of relatively thick hot shoes, a procedure that cannot be simply used with the thermoelements because thermoelement dimensions have a first order bearing on couple operation.

The analytical procedure of the present study has been the calculation of loss of thermocouple material as a result of sublimation between given/calculated thermocouple hot and cold junction temperatures and the determination of the effect of this on thermoelement cross-sectional areas. Modified thermoelement cross-sectional areas result in modified heat transfer through the thermocouple because of changes in relative cross-sectional areas of thermal insulation and thermoelements, changes in current flow through the thermocouple, and changes in thermoelement thermal conductance. Modified heat transfer rates and thermoelement dimensions in turn result in changed thermocouple operating temperatures. A general result of sublimation is an overall reduction in effective thermoelement cross-sectional areas and a consequent increase in thermocouple hot junction temperatures. Higher thermocouple hot junction temperatures mean higher values of sublimation rate and consequently further increased temperatures; the whole process is catastrophic in nature and can lead to thermocouple destruction as a result of excessive operating temperatures or complete thermoelement sublimation near the hot junctions. Counteracting the effects of sublimation and increased thermocouple hot side operating temperatures in a RTG is the reduction of fuel inventory with time as a result of isotope decay and the accompanying lowering of hot and cold side operating temperatures. Which of the two mechanisms predominates in any given case is determined by a combination of the radioisotope fuel used, beginning of life thermocouple operating temperatures, sublimation rate, thermoelement cross-sectional areas, and desired RTG life.

The present study has focused on the MHW RTG with its beginning of life thermocouple hot junction temperature of 1100°C and a required operating life of 12 years. The use of an effective thermoelement operating temperature enables the calculation of the net sublimation rate from each thermoelement at the beginning of life operating temperatures:

$$T_{Eff} = \frac{\int_{T_C}^{T_H} Tf(T)\, dT}{\int_{T_C}^{T_H} f(T)\, dT}$$

where T is absolute temperature, T_H and T_C are thermoelement hot and cold junction temperatures respectively and T_{Eff} is the effective sublimation temperature of each thermoelement. The distribution function $f(T)$ is the sublimation rate of the thermoelement material and for the 80 a/o Si - 20 a/o Ge alloy has been determined by interpolation from Figure 1 to be given by

$$f(T) = 5 \times 10^{11} e^{-\frac{51,000}{T}} .$$

The amount of material lost from each thermoelement as a result of sublimation at the effective temperature T_{Eff} over a time period Δt_1, enables the determination of new and reduced effective thermoelement cross-sectional areas at the end of that time period. Use of the new thermoelement cross-sectional areas and heat input that accounts for fuel decay in the time period Δt_1, permits the calculation of new thermocouple operating temperatures at the end of that same time period. New operating temperatures result in the calculation of a new effective sublimation temperature for the next time interval Δt_2 and new thermoelement temperatures and operating temperatures at the end of the time interval. The process may be repeated as many times as desired. For sake of rigor it is desirable to use integration techniques by using the limiting case of vanishing time intervals Δt and integrating between beginning and desired RTG end of life. It should be noted that because of the exponential character of the distribution function $f(T)$, the effective sublimation temperature T_{Eff} depends heavily on thermocouple hot junction temperature T_H and only very little on the cold junction temperature T_C. In the present study the effective sublimation temperature T_{Eff} is calculated to be only some 20°C below the thermocouple hot junction temperature T_H at any given time. It should be noted that in addition to effects of fuel decay and thermoelement sublimation, the thermocouple operating temperatures calculated in the present study also take detailed account of the effects of Peltier heat generation/absorption and Joule heating as a function of time. Due to their smallness, the effects of Thomson heat generation/absorption in the thermoelements have been neglected. Although not explicitly done here, if desired, the power output of the thermocouple may be calculated as a function of time from its dimensions and operating temperatures.

RESULTS AND DISCUSSION

The calculational model discussed in the last section has been applied to the single-stage foil insulated MHW RTG thermocouple in order to approximately assess the effects of sublimation on the performance of the generator. Although the present study only considers an individual thermocouple, the extension of the results to the RTG as a whole is obvious. Using the interpolated sublimation rate data of Figure 1 for the 80 a/o Si - 20 a/o Ge alloy, the hot junction temperatures of the MHW RTG thermocouples are shown in Figure 2 as a function of operating time for four different beginning of life temperatures, 1100, 1050, 1000 and 950°C. Figure 2 also shows the hot junction temperatures of the MHW RTG thermocouples as a function of time for the same beginning of life operating temperatures if no sublimation takes place. As already discussed, the temperatures shown in Figure 2 account for both the effects of silicon-germanium sublimation and isotope fuel decay with time. It is noted that at the beginning of life MHW RTG design operating temperature of 1100°C, the hot junction temperature increases extremely rapidly and in a short time will lead to catastrophic generator failure. Although it takes longer for this to happen at beginning of life operating temperatures of 1050 and 1000°C, it nevertheless happens in times relatively short compared to the required 12 year RTG operating time. Although sublimation effects are substantially reduced at the beginning of life operating temperature of 950°C, it is noted that after 12 years of operation they nevertheless show up even at this reduced temperature.

The results shown in Figure 2 presuppose free sublimation of the silicon-germanium thermoelements. In an actual generator structure, however, the thermoelements are usually enclosed in insulation and the sublimed species in all likelihood is not removed as fast as it is formed. The effect of the resultant baffling is to reduce the sublimation rate of the material. Inasmuch as it is nearly impossible to analytically predict the reduction of effective sublimation rate for an actual generator structure, the calculations underlying Figure 2 have been repeated for assumed sublimation rates one and two orders of magnitude below those shown in Figure 1 and used to calculate the MHW RTG hot side operating temperatures plotted in Figure 2. Figure 3 shows the results for a sublimation rate one order of magnitude lower than that used in Figure 2. It is noted that although the 1100 and 1050°C beginning of life operating temperatures still lead to catastrophic generator failure within the 12 years' operating time, it is now possible to operate the RTG at a beginning of life temperature of 1000°C without undue effects due to sublimation. The corresponding results for silicon-germanium sublimation rates two orders of magnitude lower than the maximum rates shown in Figure 1 are given in Figure 4. It is noted that although noticeable sublimation effects still occur at most of the beginning of life operating temperatures shown, the effects are relatively small, even at the 1100°C beginning of life operating temperature. The effective reduction of sublimation rate by two orders of magnitude may be accomplished in practice by baffling* of the thermoelements and may exist in well insulated generator structures without any special effort at baffling. Greater reductions in sublimation rates can probably only be obtained through the use of impervious coatings applied to the thermoelements.

CONCLUSIONS

In view of the results obtained in the present study it may be concluded:

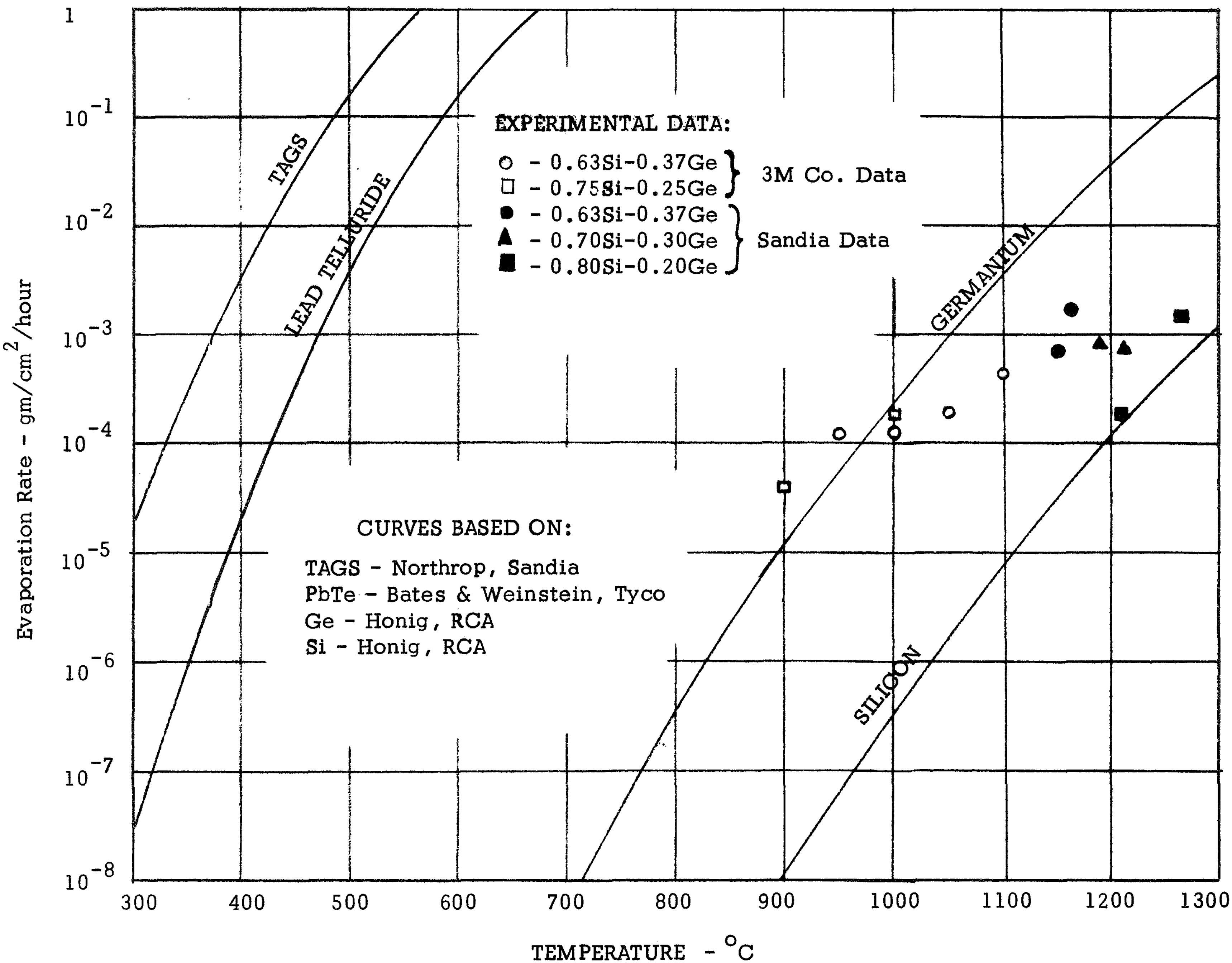
1. Operation of silicon-germanium RTG's and specifically of the MHW RTG at beginning-of-life temperatures of 1100°C is advisable only if the effective sublimation rate of silicon-germanium alloys can be reliably reduced by some two orders of magnitude below their free sublimation rate. In view of stringent reliability requirements of most RTG applications, it is questionable whether this can satisfactorily be accomplished.
2. Assuming the worst case of free sublimation of silicon-germanium, silicon-germanium RTG's should be designed for beginning of life operating temperatures below 1000°C. Because actual generator structures do in all likelihood afford some baffling, it is felt

* Norbert Elsner, GGA, Private Communication.

that a 1000°C beginning of life operating temperature may, however, not be unrealistic. On the other hand, because of reliability requirements, it is believed that higher beginning of life operating temperatures may be marginal unless sublimation can reliably be significantly reduced below its uninhibited rate.

3. Because silicon-germanium couples and generators are frequently tested under fixed conditions of operating temperature, it is possible that the mechanisms leading to catastrophic thermocouple failure are not uncovered in such tests of even fairly long duration at temperatures in excess of 1000°C. The maintenance of fixed operating temperatures does not accurately depict the fixed-heat-input type operation that thermocouples experience in an actual RTG. In the latter operating mode, thermocouple temperatures increase because of sublimation and sublimation in turn increases because of increased temperatures. Catastrophic failure thus eventually results.

4. Relative sublimation effects can be reduced, but not eliminated, by the use of relatively large silicon-germanium thermocouples. Because it is the thermocouple length to cross-sectional area ratio that has a first order bearing on thermocouple performance, it may be suggested that the larger the thermocouple, for any given value of ℓ/A, the less are the effects of sublimation. Very small thermocouples should be avoided, if possible.



1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
Evaporation Rate - gm/cm^2/hour
TAGS
LEAD TELLURIDE
GERMANIUM
SILICON
EXPERIMENTAL DATA:
○ - 0.63Si-0.37Ge
□ - 0.75Si-0.25Ge
3M Co. Data
● - 0.63Si-0.37Ge
▲ - 0.70Si-0.30Ge
■ - 0.80Si-0.20Ge
Sandia Data
CURVES BASED ON:
TAGS - Northrop, Sandia
PbTe - Bates & Weinstein, Tyco
Ge - Honig, RCA
Si - Honig, RCA
300
400
500
600
700
800
900
1000
1100
1200
1300
TEMPERATURE - °C

Figure 1

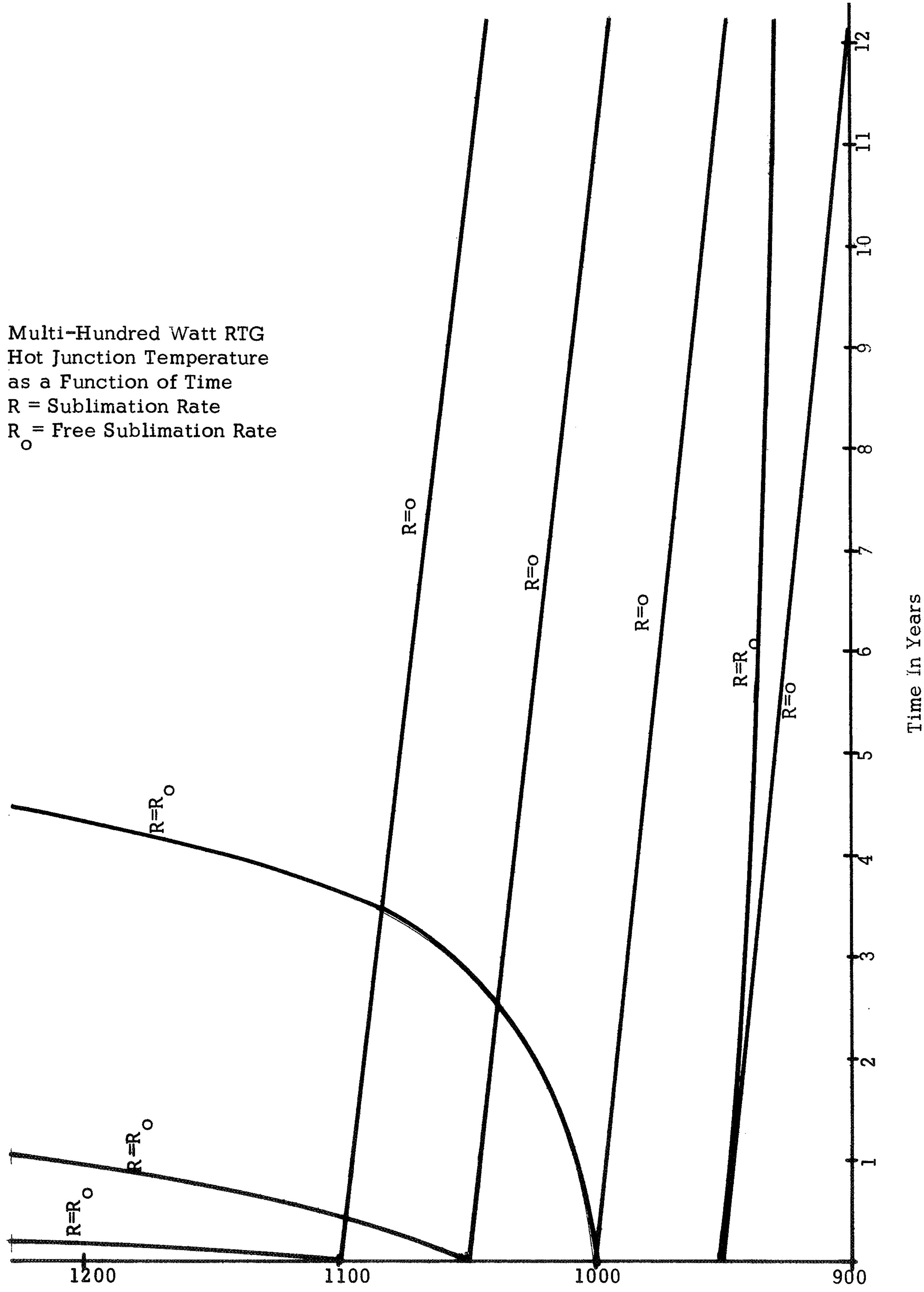
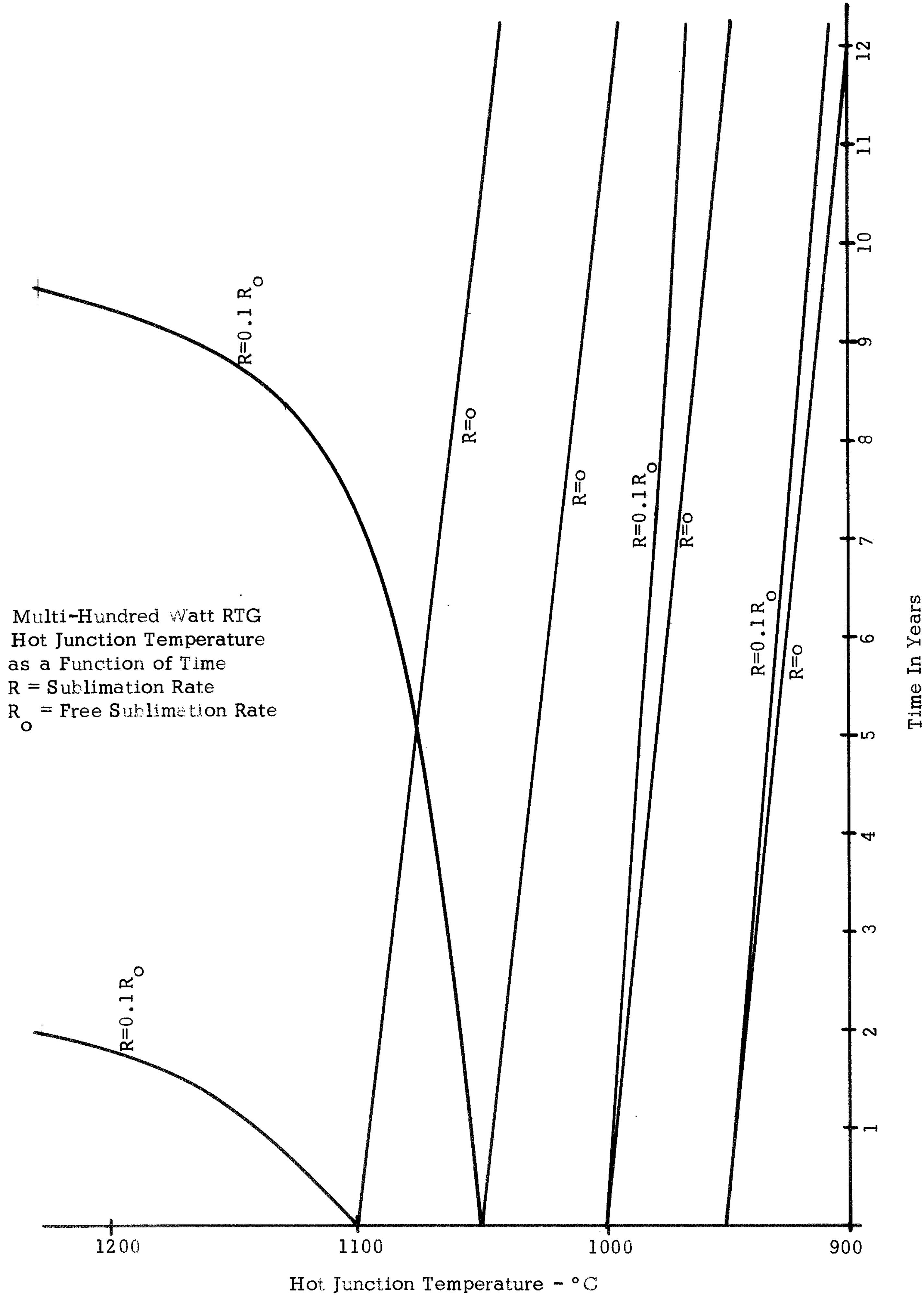

Multi-Hundred Watt RTG
Hot Junction Temperature
as a Function of Time
R = Sublimation Rate
R o = Free Sublimation Rate
R=o
R=o
R=o
R=Ro
R=o
R=Ro
R=Ro
R=Ro
Time In Years
1
2
3
4
5
6
7
8
9
10
11
12
1200
1100
1000
900
Hot Junction Temperature - °C

Figure 2



Multi-Hundred Watt RTG
Hot Junction Temperature
as a Function of Time
R = Sublimation Rate
R o = Free Sublimation Rate
R=0.1 R o
R=o
R=o
R=0.1 R o
R=o
R=0.1 R o
R=o
R=0.1 R o
1200
1100
1000
900
Hot Junction Temperature - °C
1
2
3
4
5
6
7
8
9
10
11
12
Time In Years

Figure 3

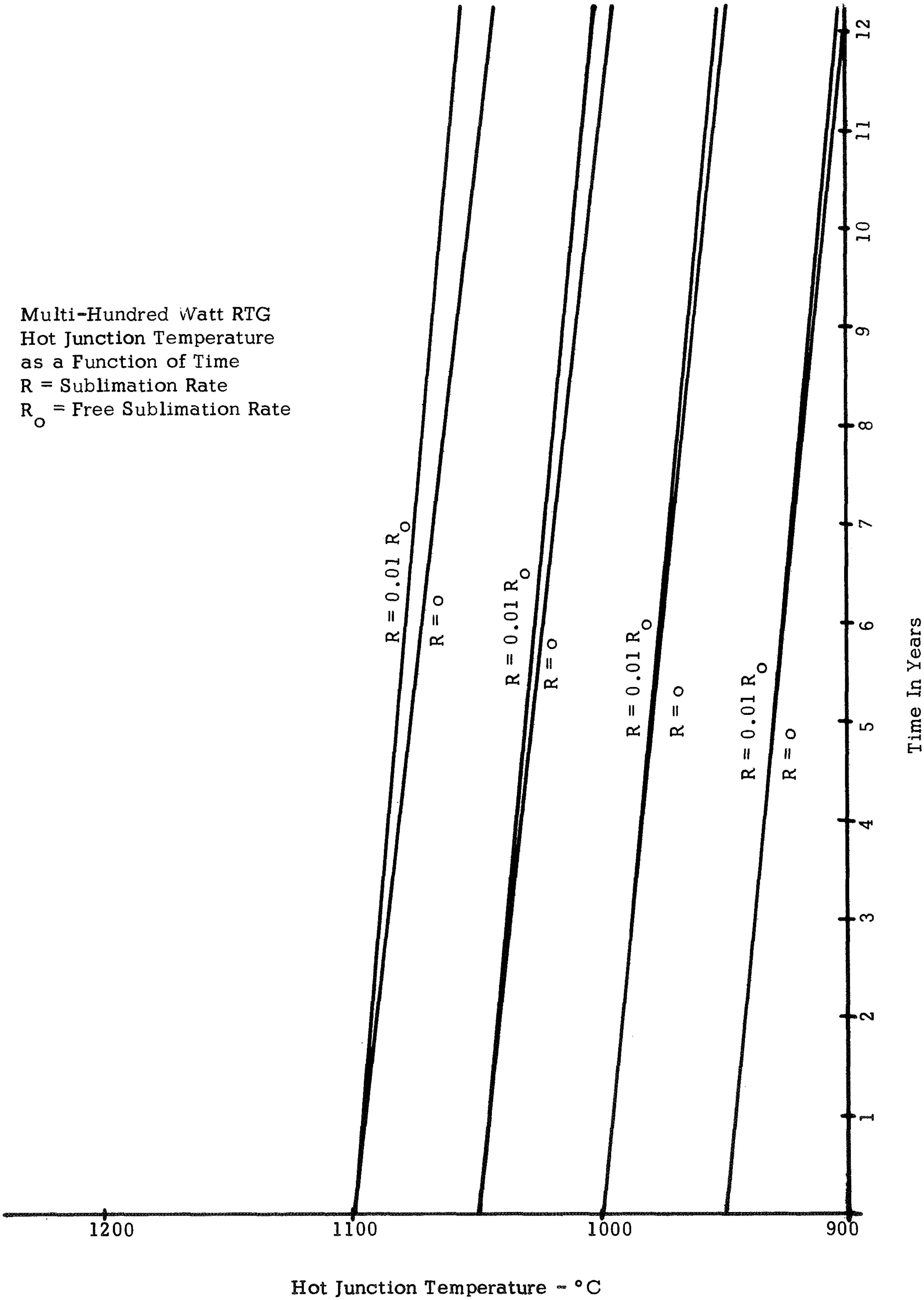

Multi-Hundred Watt RTG
Hot Junction Temperature
as a Function of Time
R = Sublimation Rate
R_o = Free Sublimation Rate
R = 0.01 R_o
R = o
R = 0.01 R_o
R = o
R = 0.01 R_o
R = o
R = 0.01 R_o
R = o
1200
1100
1000
900
1
2
3
4
5
6
7
8
9
10
11
12
Time In Years
Hot Junction Temperature - °C

Figure 4