

DOE/ET/33003--T5 M&R 959

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THE COPPER-SELENIDE SYSTEM

P-TYPE TPM-217

EM 341-013 *AL0376 ET33003* April 1977

by

G. Stapfer
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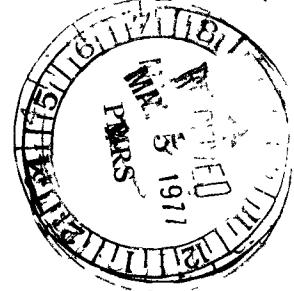
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FOREWORD

The use of thermoelectric generators to supply the electrical power for unmanned space probes has demonstrably proven to be reliable and will undoubtedly continue to be the primary source of electrical power for many future missions. Up to the present time, all of these generators used either lead-telluride or silicon-germanium for the thermoelectric material alloy. The intention for most all of the future generators is, however, the use of the latest developed material, namely the selenides. This report is an attempt to summarize the particular peculiarities of this material as they differ markedly from the conventional thermoelectric materials and are generic to the selenide system only.

THE COPPER-SELENIDE SYSTEM

P-TYPE TPM-217

Unmanned scientific space probes require electrical power to operate the spacecraft; the power ranges from 200 watts to 1000 watts. For missions which are directed away from the sun, or in which the flight path intercepts areas of high nuclear radiation, solar power, i.e., photovoltaics, becomes impractical. For these kinds of missions, the ideal power source is the Radioisotope Thermoelectric Generator (RTG). Many missions which are currently under consideration by NASA fall within this category, and the use of RTGs is inevitable. In the past, the thermoelectric uncouples which convert the heat generated by the isotope decay into usable electricity have been of two types: one, the lead-telluride system which operates at intermediate temperatures ranging from 500°C to 150°C; and two, the high temperature silicon-germanium systems which operate between 1000°C and 300°C. For all of the upcoming missions, a new type of material is being considered; the selenide system which operates between 900°C and 150°C. The major advantage of this new thermoelectric material over its predecessors is the much higher efficiency with which heat is converted into useful electricity. This increased conversion efficiency provides about 75% more electrical power for the same amount of very expensive radioisotope fuel (Pu-238), thus significantly reducing the cost of the conversion system.

One major difference of this new thermoelectric conversion material is that the 'n' and the 'p' leg of a uncouple are made of a different alloy rather than being merely positively or negatively doped identical materials as was the case for the Pb/Te and the Si/Ge systems. The n-element consists of a gadolinium-selenide (Gd_2Se_3) alloy, while the p-leg is a copper-selenide material ($Cu_{1.97}Ag_{0.03}Se_{1+y}$), with variations in the amount of excess Se ($Se + y$). While each of the two materials possesses its own different set of characteristics, this

report is to highlight the peculiarities of the p-type alloy, primarily as it is the only one of the two materials which has been made available to JPL for evaluation at the present time.

The mechanical, chemical and electrical properties of most material alloys differ to a greater or lesser extent for different compositions of the same alloy. In the developing process of a thermoelectric material, an alloy composition is selected to possess a set of characteristics which will be most advantageous for efficient power conversion, compatible with long-term operation of high temperatures. In the case of the copper-selenides, this selection of the desired composition becomes somewhat more complicated; this material possesses the peculiarity of having its composition altered, or modified, by the presence of a current gradient across the material. In addition, the composition will also slightly depend upon temperature gradients. Because of this, not only do the thermoelectric performance parameters, such as Seebeck voltage, resistivity and thermal conductivity, depend on temperature and an initial alloy composition, but they are also subject to large modifications by current gradients and temperature gradients. This peculiarity of the material poses an additional complication in evaluating the performance data from a single element to a full-up generator. Since "standard" property data are not really "standard", but are subject to gradients, which in turn are dictated by geometry and temperature profiles, the design as well as the performance prediction of an RTG becomes rather involved.

Theoretically, a large compositional range (in percentages of excess selenium) of copper-selenide alloys can be synthesized; each with its own set of properties. In practice, however, the bonding of this alloy to a copper cold shoe fixes the composition to a single unique value determined by temperature. In the absence of either current or temperature gradients, the bonded material (bonded to a copper reservoir so to speak) will follow a unique composition value as its

temperature is varied. This composition, expressed in percentage of excess selenium as a function of material temperature is illustrated in Figure 1. The data for this figure are based on Reference 1 for the low temperature and Reference 2 for a point at 500°C and 800°C.

If it were not for the temperature and current gradients which develop across the thermoelectric leg, the composition of the material would be uniquely determined by the temperature of the cold end which is bonded to copper. As an example, a leg operating at a cold end temperature of 150°C would exhibit a uniform 0.07% excess selenium material composition. The thermoelectric properties corresponding to this composition could now simply be determined as a function of temperature for the remainder of the p-leg. Both the temperature and the current gradient (and without such gradient, no useful power can be developed) shift the composition of the material towards a higher content of Se (to the right-hand side of Figure 1). The change of composition due to the temperature gradient only is rather small and is omitted from this analysis. However, since the composition is very strongly dependent upon the current gradient, its effect must be included in any data or performance analysis.

The relationship of material composition to the current gradient has been determined by the 3M Company (Ref. 2) as follows:

$$\Delta n = 0.0095 \frac{il}{A} \quad (1)$$

where Δn = the increase in excess selenium in percent

$\frac{il}{A}$ = current gradient, in amp/cm

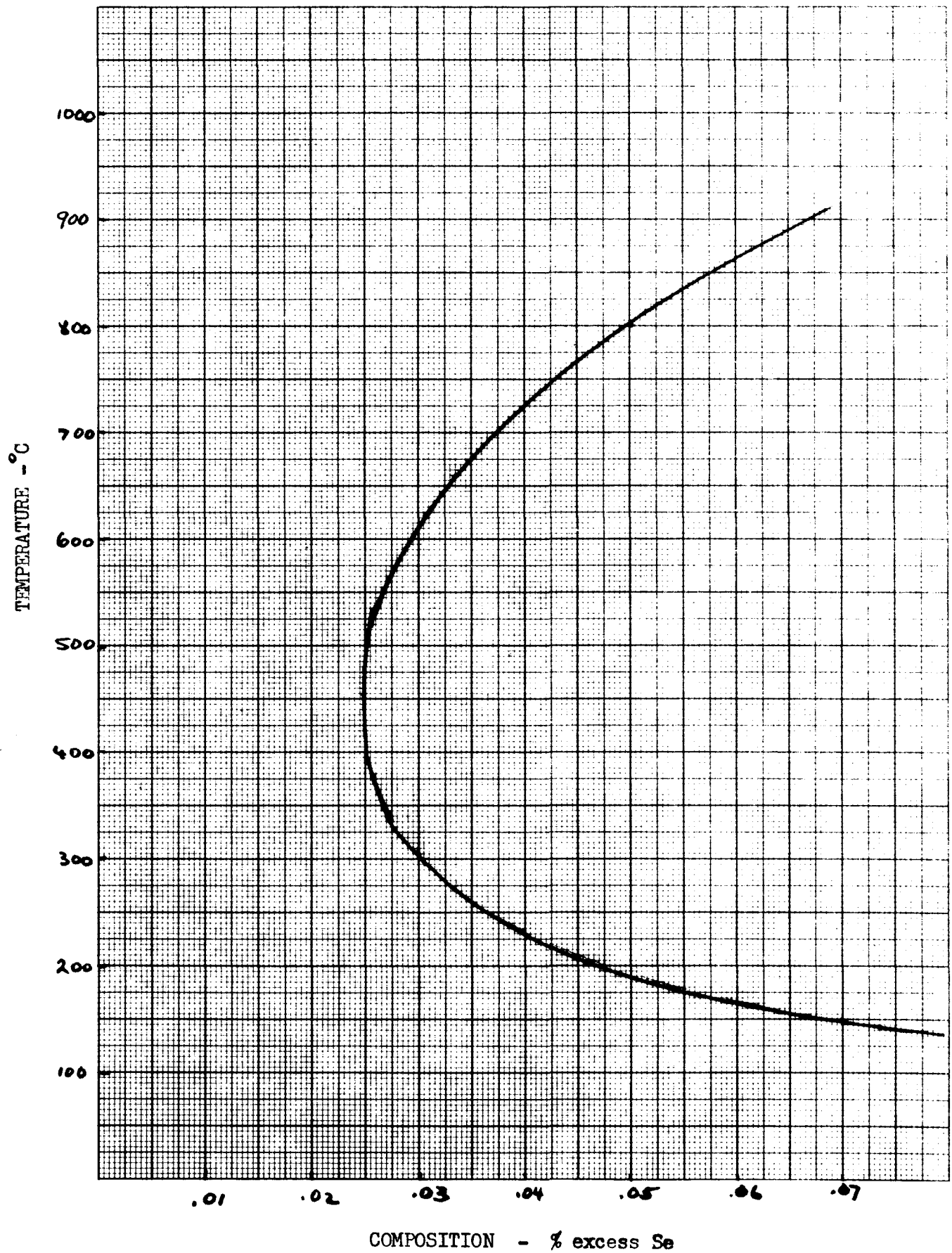
i = current, amps

l = length of material or leg

A = cross-sectional area of material or leg

With the aid of Figure 1 and the above expression, the exact composition at

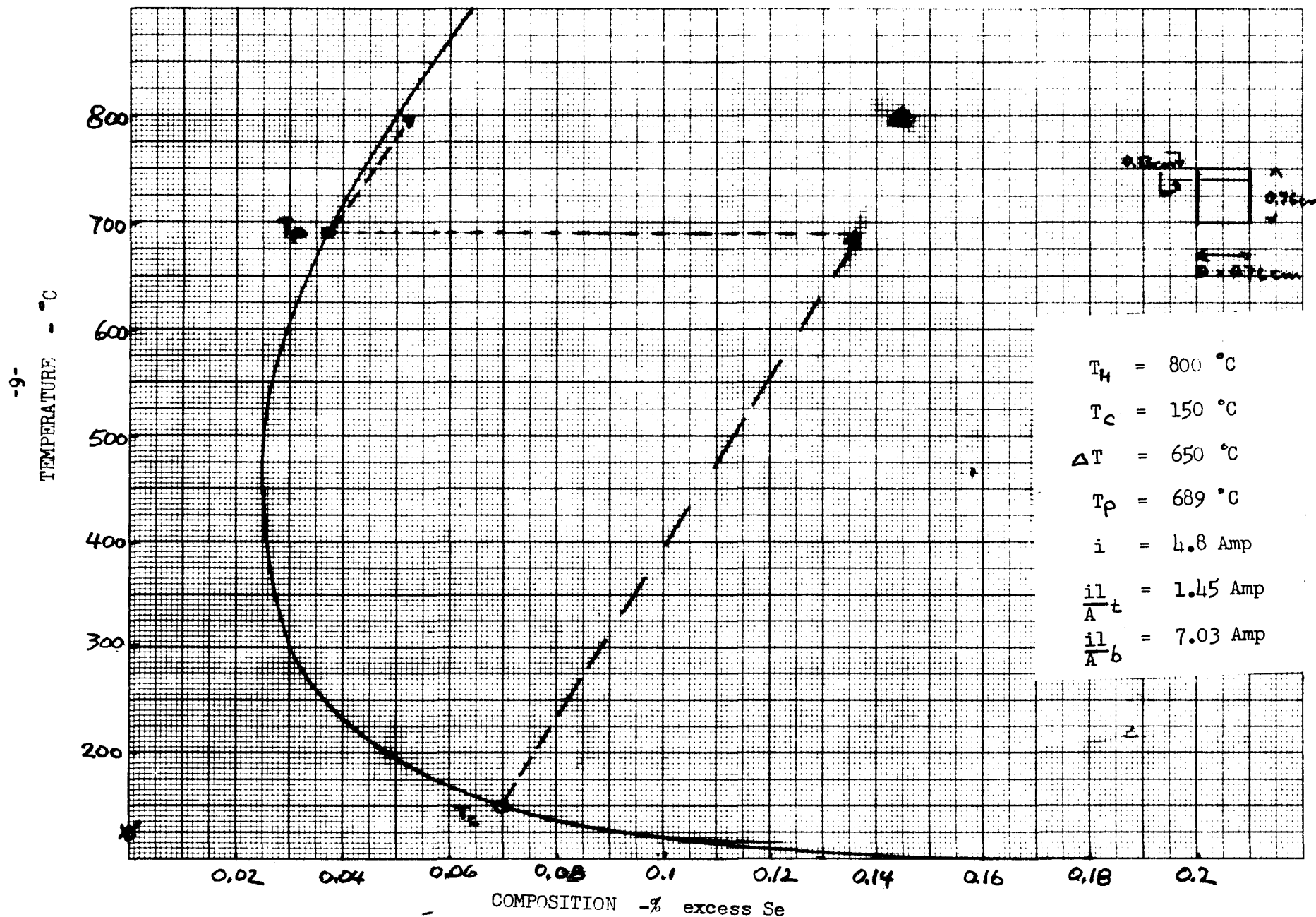
Figure 1. Equilibrium Composition of p-type TPM Material When Bonded to Copper (Isothermal - Zero $\frac{il}{A}$)



any point along the leg for a fixed geometry, operating temperature and steady state current can now graphically be determined. This composition is shown in Figure 2 for a typical p-leg with the dimensions and operating temperatures as shown. The p-leg shown in the figure is a singly partitioned leg. The reason for the partitioning will be discussed later on. Starting with the cold end of the leg, with a composition of 0.07% excess Se, the composition is shown to linearly increase in excess selenium. The temperature of the partition was determined to be 690°C (assuming a simple linear temperature profile across the leg, an assumption which is reasonable but not strictly correct, since the thermal conductivity along the p-material changes with temperature). The material at this temperature (just below the partition) has a composition of 0.136% excess selenium. At the same temperature (assuming a zero temperature drop across the partition), just above the partition the material returns to the much lower value of excess selenium as it is in equilibrium with the copper again at this point. The partition which is a tungsten foil is coated with copper on the side facing the hot side. An increase of selenium again occurs between the partition temperature and the hot side temperature (800°C), however this excess selenium is now referenced to the lower value corresponding to the partition (0.035%). The actual composition at the hot side of the leg therefore becomes considerably less selenium-rich due to the partitioning than a nonpartitioned leg would be. The composition of such a leg (nonpartitioned) is also shown for the same geometry and operating characteristics (indicated by the triangular symbol).

The reasons for partitioning the p-leg and thus changing the composition of the leg are twofold: 1) the mechanical properties, namely the creep strength of the material, degrade with increased selenium content; 2) the weight loss rate due to sublimation increases with an increase of excess selenium. Both of these mechanisms are highly undesirable, particularly for high temperature applications.

Figure 2. Equilibrium Composition of a Singly Partitioned Element Bonded to Copper at a Current of 4.8 Amps



In addition to the mechanical and thermophysical property changes, the basic thermoelectric properties, i.e., Seebeck voltage, resistivity and to a minor extent the thermal conductivity, also change as the selenium composition is varied.

The effect which the current gradient has on the weight loss rate of this material has been documented in Reference 3 and will be discussed further in a later section of this report. The changes in thermoelectric properties which are due to material composition are graphically illustrated in Figure 3 which plots the resistivity of p-type material versus operating temperature for three different material compositions. The data for the two lower curves (for an excess selenium content of 0.1% and 0.18%) are given directly in Reference 4, while the third curve is based on average performance data (in-gradient data) from the same reference. Figure 4 shows the same basic data plotted as a function of selenium composition for different temperatures. With the aid of Figure 2 and Figure 4, the resistivity along the length of the element (which is synonymous with the temperature gradient along the leg) can be plotted. Using Figure 2, the composition of the element is a function of temperature, thus the axial position is determined. Figure 4 shows the resistivity of the element as a function of temperature and composition. The resistivity at any point of the leg as determined from the two plots is shown in Figure 5 for a typical p-leg. The leg operates at 800°C at hot side and 150°C on the cold side and a uniform temperature profile is assumed between the hot and the cold side. The very dramatic increase of resistivity which occurs as a result of the segmenting is obvious. The resistivity which would result in a nonsegmented leg is also shown (at the 800°C point) by a dotted extension and the triangular symbol.

The resistivity of the same segmented leg but without current gradient is also shown in the figures. The current gradient is shown to "improve" the resistivity parameter as the integrated leg resistance would be lower without

Figure 3. Resistivity Versus Temperature for Different Compositions of p-type Selenide Material (Zero $\frac{il}{A}$)

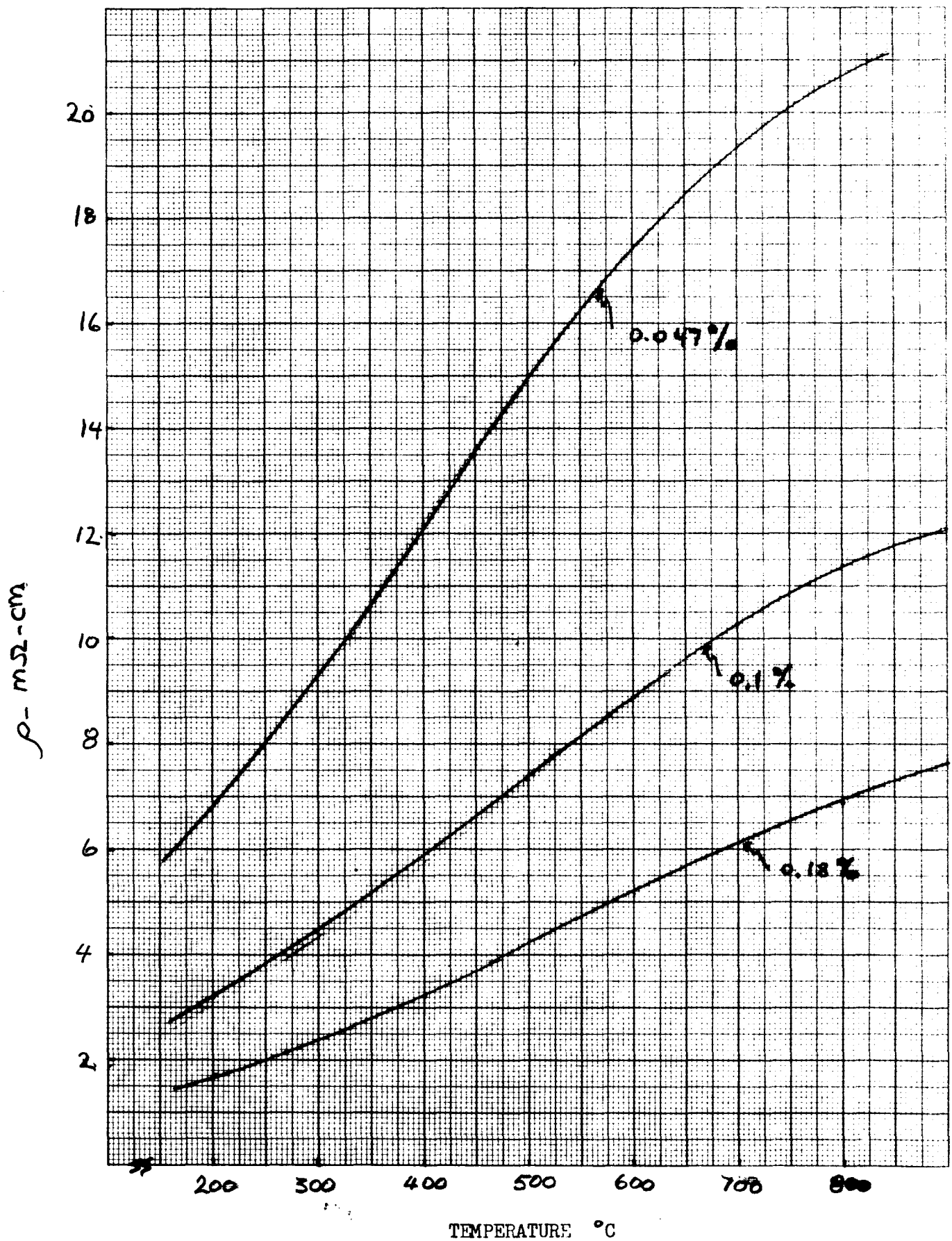


Figure 4. Resistivity Versus Composition for Different Temperatures (p-type Selenide)
(Zero $\frac{il}{A}$)

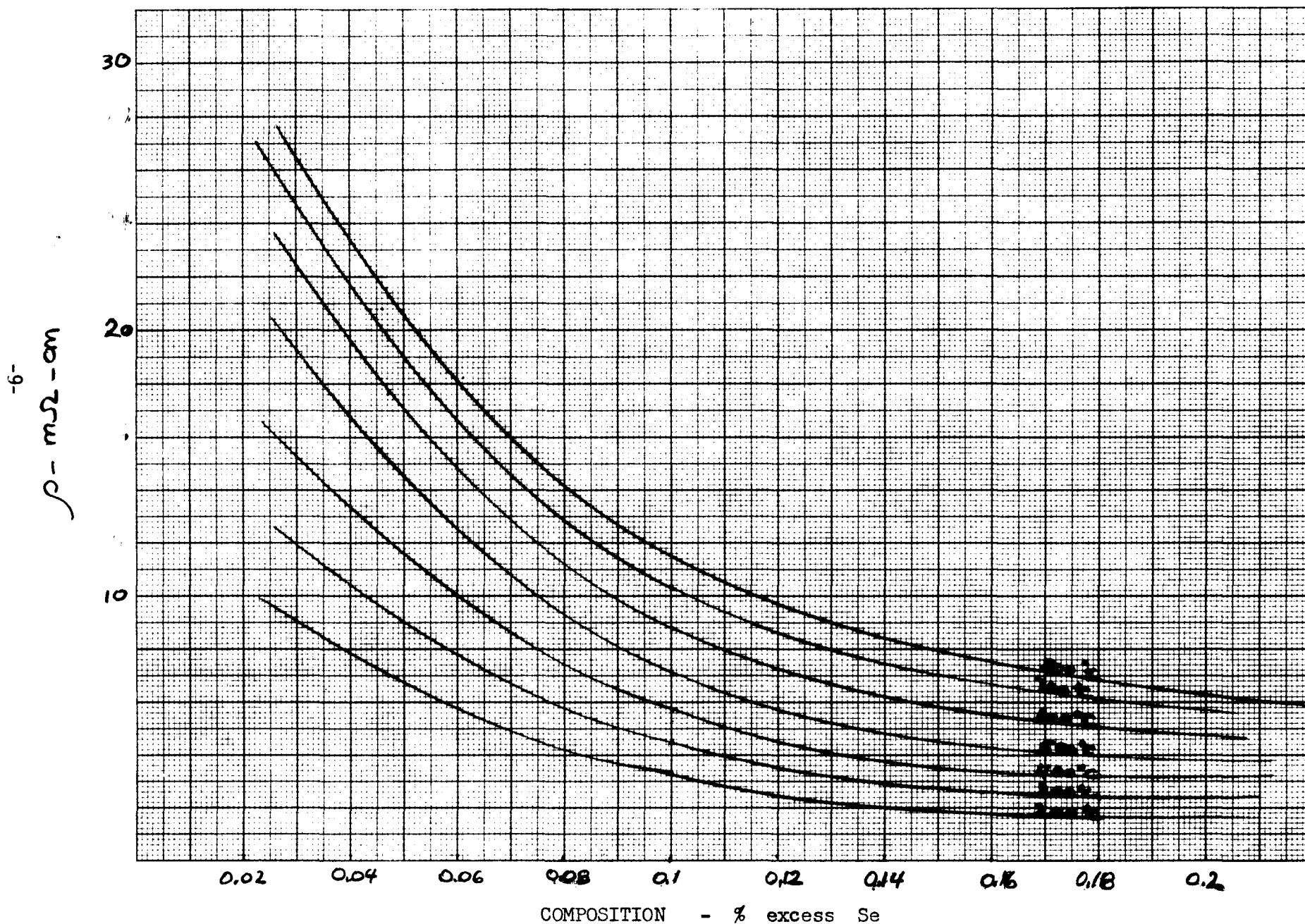
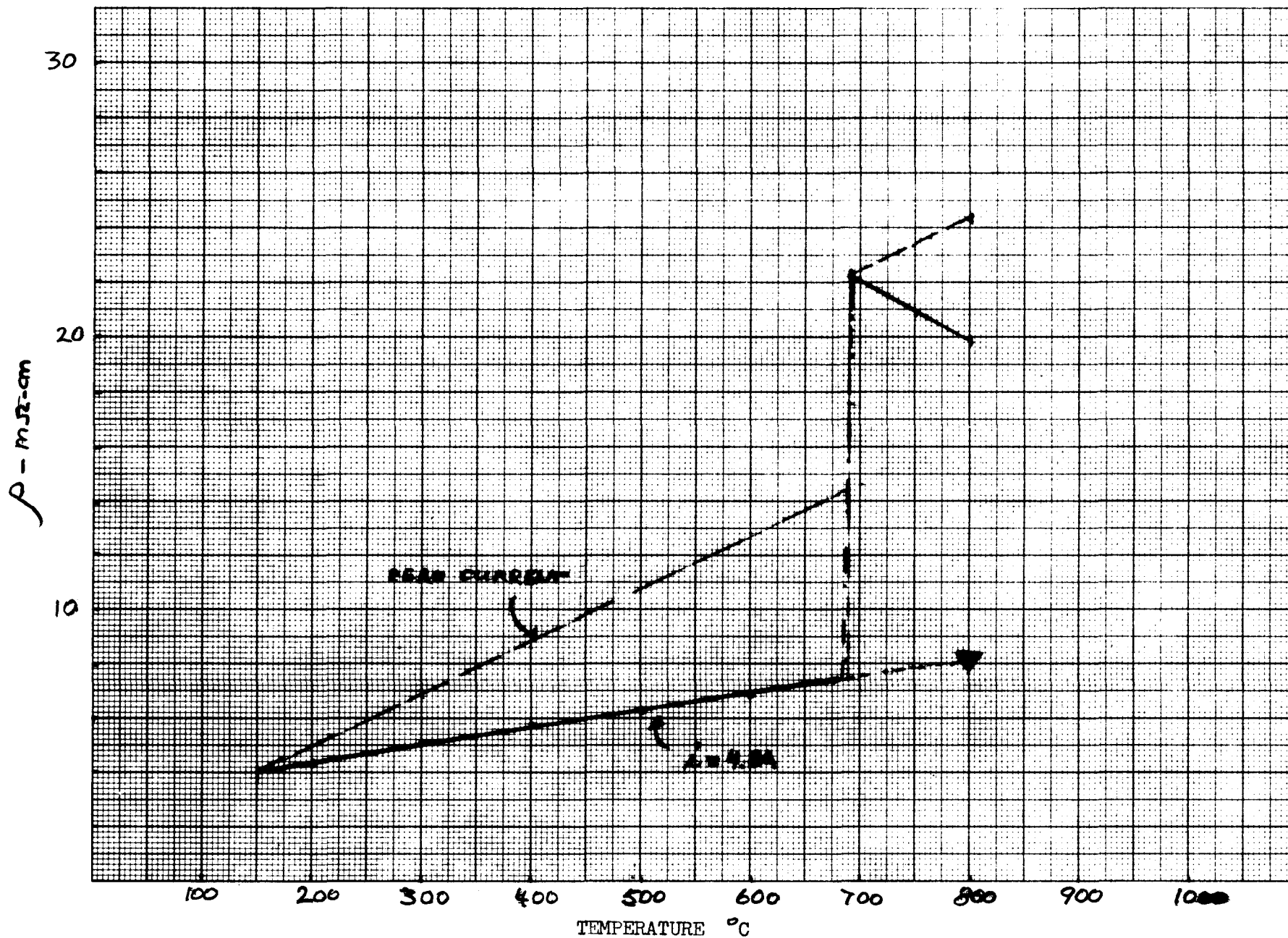


Figure 5. Resistivity Versus Temperature for a p-type Selenide Leg, Singly Partitioned at a Current of 4.8 amps



this gradient.

Similar data and curves have been developed for the Seebeck voltage. Although this parameter is less sensitive to compositional changes, its exact behavior as the selenium content is varied is not as clear as one would desire. Figure 6 shows the Seebeck voltage versus temperature, again for the same three different material compositions. The same reference (Ref. 4) is the source for this data. The area of primary concern as to the accuracy of the data is near the temperature extremes for the lowest composition (top curve); this area is shown dashed. Figure 7 cross plots this same data to visualize the Seebeck voltage parameter sensitivity with compositional changes. The same technique which was described above is again applied to obtain the localized Seebeck voltage in a p-leg operating between 800°C and 150°C . This is shown in Figure 8. The segmenting of the p-leg has a much lesser effect on the Seebeck voltage parameter than it had on the resistivity shown earlier. The current gradient effect is also shown in the figure, and as it tends to reduce the Seebeck voltage, it may be termed a "deteriorating" effect as opposed to the previously shown "improvement" of the resistivity.

The universal parameter indicative of the real performance of any thermoelectric material is the figure of merit (z) which is the ratio of the square of the Seebeck voltage and the product of resistivity and thermal conductivity. The point values of all of these parameters are tabularized as a function of temperature in Table 1. Two different thermal conductivity values and therefore z values are shown in the table. The column headed "3M Data" is based on data obtained from Reference 4, while the JPL values are based on measurements made at JPL as part of the selenide technology program (Ref. 3). Both sets of thermal conductivity values are assumed to be independent of the material composition change caused by the current gradient. This assumption was made due to a lack of data on this dependence, which is however felt to be of a secondary effect

Figure 6. Seebeck Voltage Versus Temperature for Different Compositions of p-type Selenide (Zero $\frac{il}{A}$)

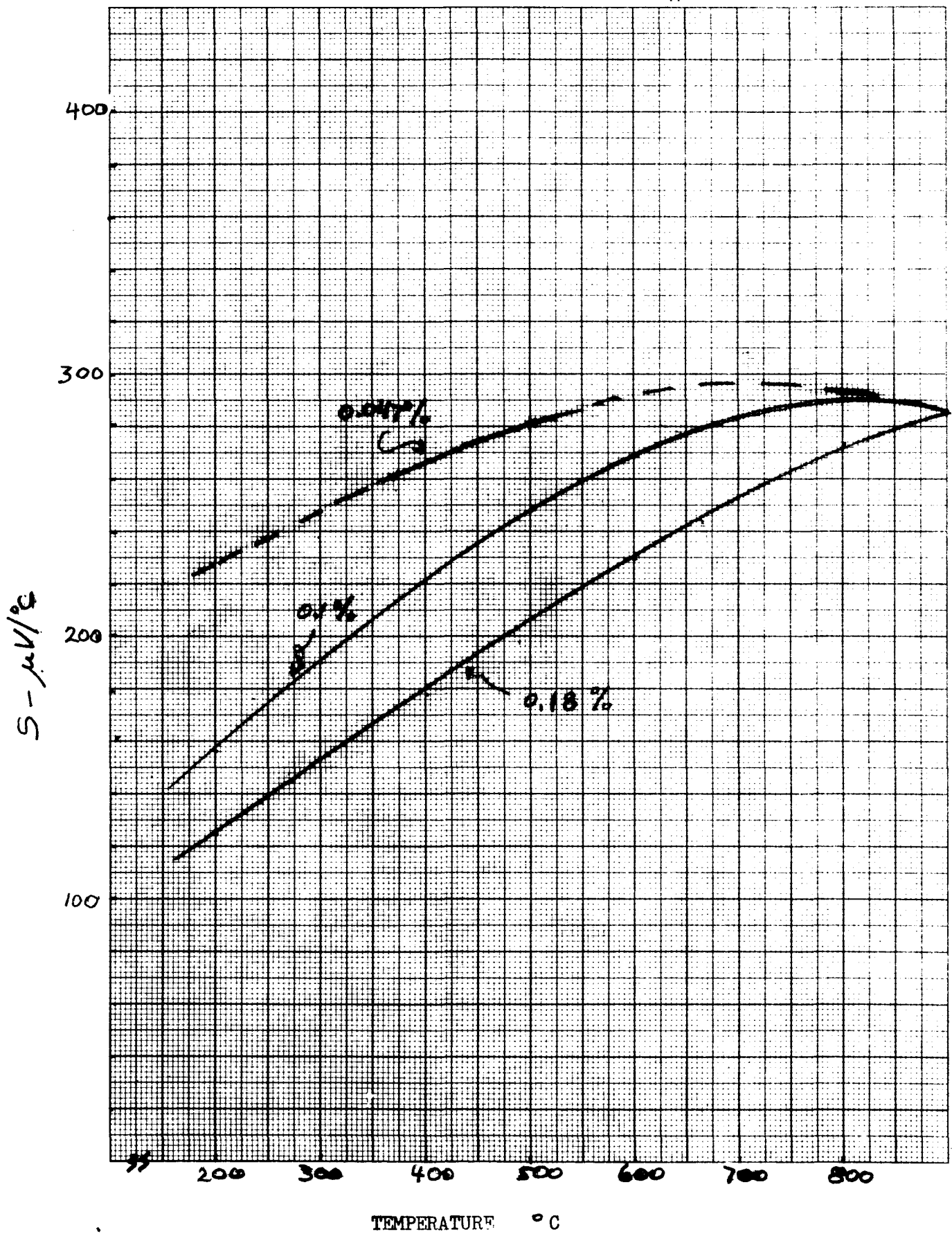


Figure 7. Seebeck Voltage Versus Composition for Different Temperatures (Zero $\frac{dI}{dA}$)

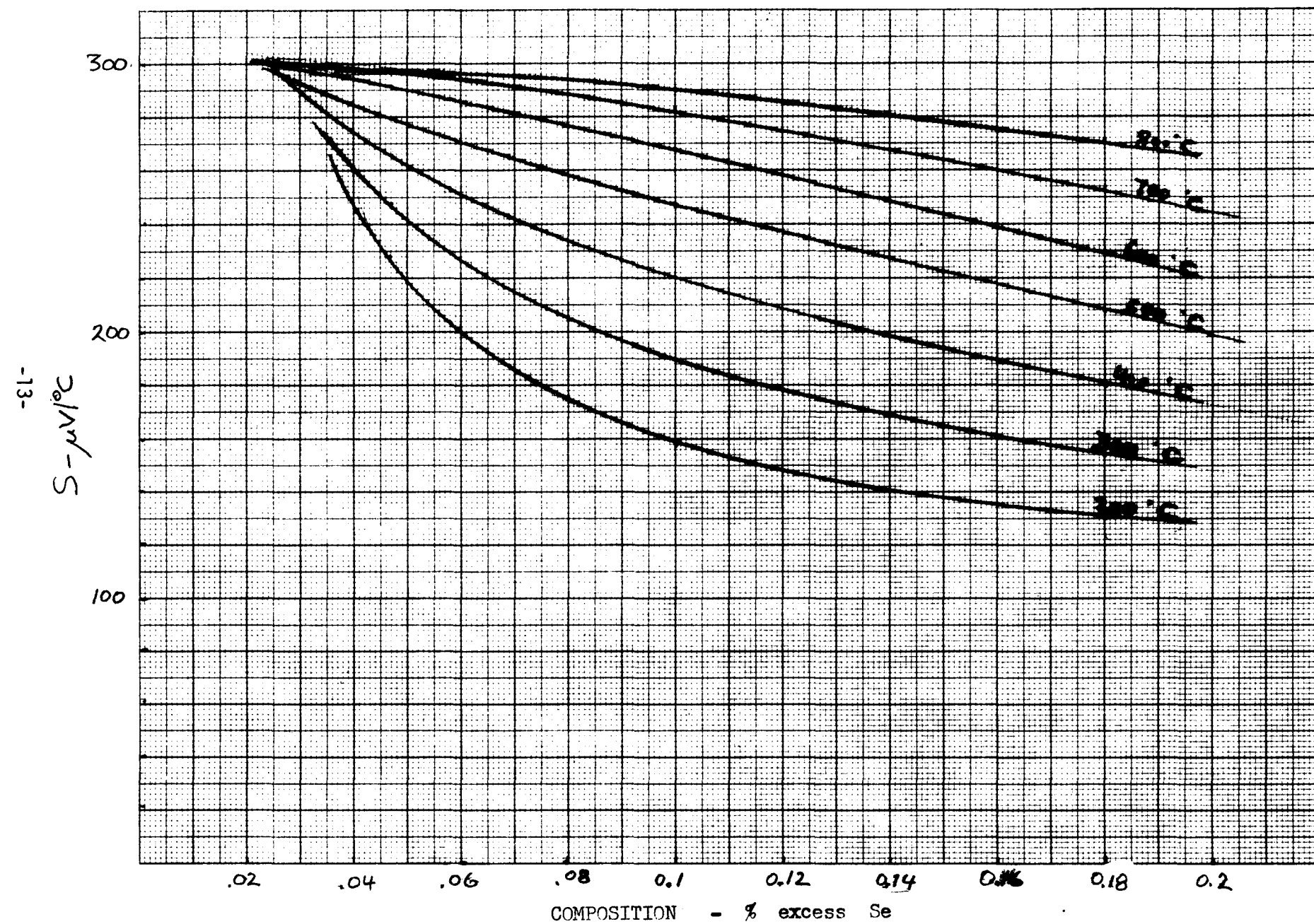


Figure 8. Seebeck Voltage Versus Temperature for a p-type Selenide Leg,
Singly Partitioned at a Current of 4.8 Amps

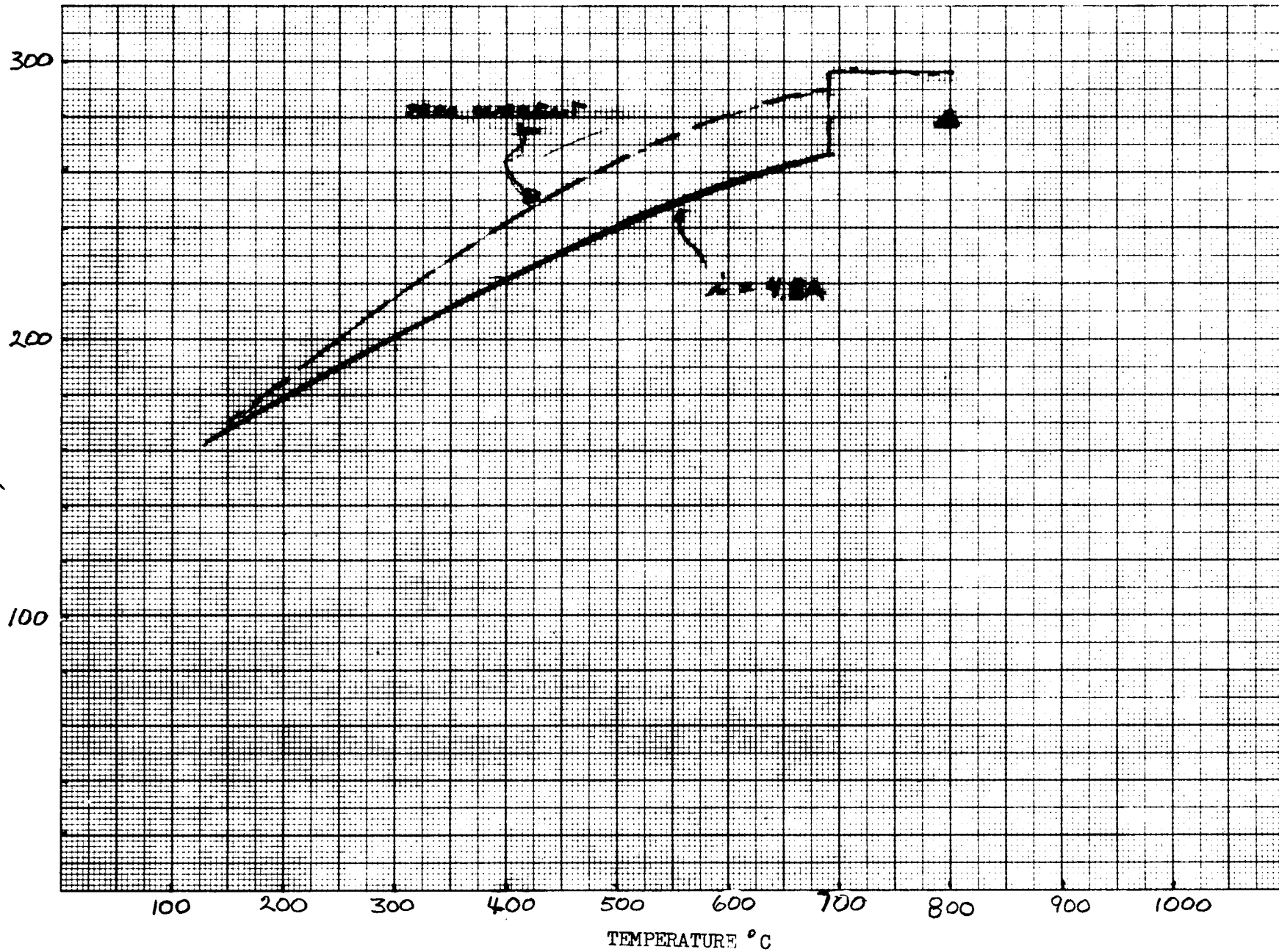


Table 1. Thermoelectric Properties of p-type Selenide at 4.8 Amps^{*}

Temp. °C	Seebeck V/°C	Resistivity mohm-cm	Thermal Cond. JPL mW/cm°C	Thermal Cond. 3M mW/cm°C	Figure of Merit JPL 10 ³	Figure of Merit 3M 10 ³
200	178	4.4	8.2	7.5	0.88	0.96
300	200	5	7	6.8	1.14	1.17
400	220	5.8	6.8	6.5	1.23	1.28
500	240	6.4	7.3	6.5	1.23	1.38
600	255	7	9	6.8	1.03	1.37
690	266	7.4	10.7	7.5	0.89	1.23
690	296	22.2	10.7	7.5	0.37	0.53
800	296	19.8	13.5	8.8	0.33	0.5
800 ⁺	280	8	13.5	8.8	0.73	1.

^{*} Leg geometry: diameter = 0.76 cm, top segment = 0.13 cm, bottom segment = 0.63 cm.

⁺ Assuming same leg geometry but no partition (4.8 Amps).

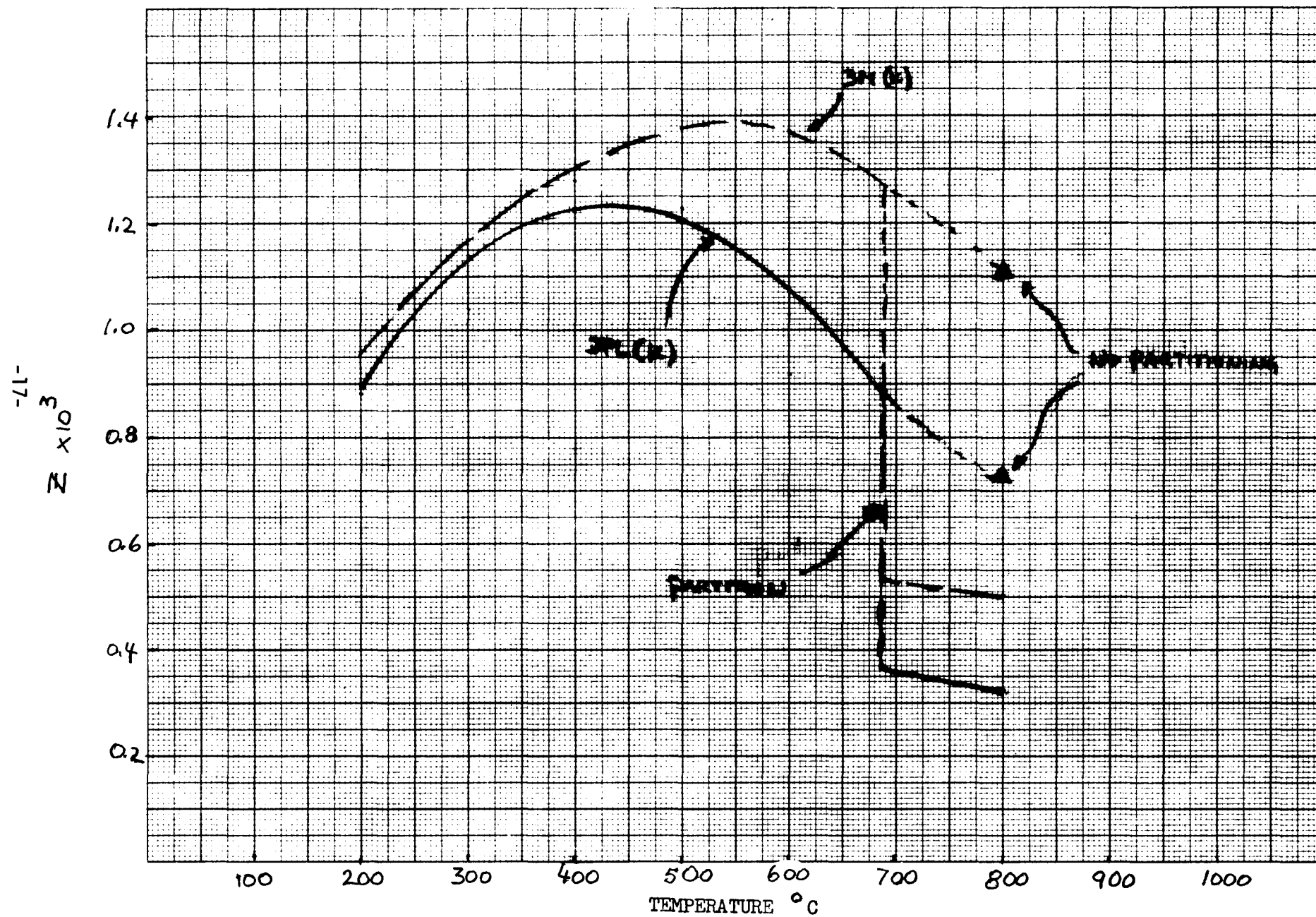
(Ref. 2). The two sets of values given at 690°C pertain to the material immediately below and above the partition (it should be remembered that the partition causes a step change in the material properties). The graph of the z values is shown in Figure 9 as a function of temperature.

The data which are based on the 3M thermal conductivity values are shown dashed, and reflect the lower values of this parameter and result in the larger z value. The triangular end points (at 800°C) again indicate the characteristic of a nonsegmented leg. The very substantial decrease in the z values resulting from the partition is apparent, and results regardless of which thermal conductance value is used.

The less than optimum performance which results from partitioning the p-leg raises the question as to its advisability. The penalty incurred in the electrical performance is however more than compensated for by the advantages which are gained in the thermophysical properties such as a decrease in material weight loss. As an example, the weight loss rate of a p-leg (i.e., the loss rate of the material adjacent to the hot junction) operating at 800°C is reduced by a factor of approximately 25 by the single partition (see Ref. 3). Another way of comparing the advantages is to realize that partitioning will allow either 1) a 25 times longer lifetime at identical temperatures or 2) for identical lifetimes, an increase of almost 200°C in the operating temperature. Either of these two factors will more than compensate for the decreased performance which is caused by the segmenting process.

However, there is an inherent degradation mechanism related to the material composition change caused by the current gradient. The typical RTG power conditioning system is designed to operate the RTG at a constant output voltage. As the available output power from the RTG decreases due to isotope decay (and possibly other mechanisms), at this constant voltage a lower output current will result. This in turn will decrease the current gradient across the p-leg, con-

Figure 9. Figure of Merit Versus Temperature for a p-type Selenide Leg,
Singly Partitioned at a Current of 4.8 Amps



sequently changing the material composition. This change in composition will increase the Seebeck voltage but also increase the resistivity. Depending of course on the relative changes of these two parameters, the resultant z value will either increase or decrease. To gain a measure of the direction which the z value will take, an extreme case (i.e., zero current gradient) was evaluated. For example, at a temperature of 600°C , the Seebeck voltage will increase by 9% while the resistivity at the same temperature will increase by 46%. The result will be a net decrease of the z value of approximately 20%. In a real RTG, the change would be much smaller of course, but it would definitely be a decrease, and therefore it must be considered a degradation mechanism. The problem could possibly be circumvented by a redesign of the Power Conditioning System which could be changed to a constant current type if the degradation rates involved were to warrant a change in concept.

From the information which has been presented in this report, it can readily be realized that the successful application of the selenide thermoelectric materials will to a large extent hinge on a thorough understanding of the exact behavior of this system. Since all of the parameters are sensitive to current gradients and to a lesser extent also to the thermal gradients, a meaningful generator performance prediction will most certainly require the application of a computer code. The development of such a code has already been initiated. Basically, it will follow and track all of the synergistic changes which occur during normal generator operation. As this code develops, applicable input data will continuously be incorporated and updated as such data become available from experiments which are conducted at JPL as well as other government agencies and corporate laboratories.

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