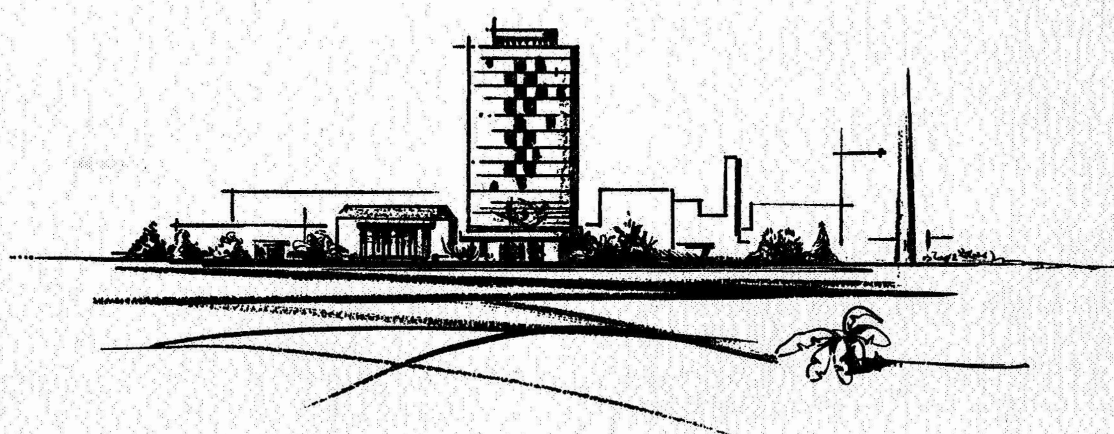
RESEARCH REPORT

AN ADVANCED THERMOELECTRIC
LIFE TEST AND EVALUATION STUDY
(Phase II)

(December 27, 1968 - June 30, 1969)

CONTRACT NO. NAS5-11644



BATTELLE MEMORIAL INSTITUTE

COLUMBUS LABORATORIES

FINAL REPORT

on

AN ADVANCED THERMOELECTRIC LIFE TEST AND EVALUATION STUDY (Phase II)

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CONTRACT NO. NAS5-11644

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ABSTRACT

A test apparatus has been designed and fabricated for the performance of thermoelectric couple life tests and efficiency measurements at constant thermal input power. Particular emphasis was placed on the development of the thermal insulation system in order to limit parasitic heat losses from the heat source to less than ~15 percent, hence, simulating operating conditions typical of radioisotope-fueled thermoelectric generators.

The apparatus described has been used to measure the energy-conversion efficiency of SiGe-PbTe segmented thermoelectric couples operating at cold- and hot-junction temperatures of 325 K (52 C) and 1200 K (927 C), respectively. The results of these measurements indicate that SiGe-PbTe segmented couples operating in this range are capable of conversion efficiencies of up to 9.8 percent, a significant improvement over either of these two thermoelectric materials operating individually.

INTRODUCTION

Thermoelectric materials are a special class of highly doped semiconductors which have been optimized for the efficient conversion of thermal energy into electrical energy. The semiconducting materials suitable for use in thermoelectric energy-conversion devices must possess (1) a high thermoelectric power (Seebeck coefficient) and electrical conductivity, (2) a low thermal conductivity, and (3) a high degree of stability while operating at elevated temperatures (500 to 1000 C).

The experience of both system contractors and experimental investigators has indicated the need for uniform procedures for tests and measurements of thermoelectric materials and components. The standardization of the procedures for the measurement of output power stability (i.e., life testing) and energy-conversion efficiency is especially important since the performance data derived from these tests are the basis for the design, development, and fabrication of systems employing thermoelectric converters. A detailed examination of life-testing and efficiency-measurement techniques was conducted and from which it was concluded that (1) life testing should be performed under conditions of constant or controlled thermal input power (in contrast to constant hot- and cold-junction temperatures) in order that the test data reflect changes in the thermal conductance of the thermoelectric couples and (2) conversion-efficiency measurements accurate to within $\sim$7 percent may be performed using calibrated heat-flux transducers, hence, eliminating the necessity for complicated heat meters and their associated thermal guarding.

Prior thermoelectric couple life-testing techniques, which evaluated electrical output power as a function of time at constant hot- and cold-junction temperatures, were, by design, insensitive to changes in the thermal conductance of the test specimen. These changes in thermal conductance are related to changes in the "effective" dopant concentration of the semiconducting materials which often result from (1) loss of dopant by sublimation, (2) redistribution of dopant due to thermal diffusion, and (3) chemical reaction of the dopant and/or semiconductor with contaminants present in the environment of the thermoelectric materials.

An example of the importance of monitoring the thermal conductance of thermoelectric couples is provided by comparing the output-power stability of couples containing 3p-PbSnTe under conditions of fixed operating temperatures or fixed thermal input power. Specifically, couples containing 3p-PbSnTe elements exhibit, under conditions of constant hot- and cold-junction temperature (1) a decreasing Seebeck voltage and electrical resistivity and (2) a stable output power. Subsequent studies* of the relationship between the electrical and thermal properties of semiconductors undergoing degradation revealed that the observed changes in the Seebeck voltage and electrical resistivity were attended by significant changes in the thermal conductivity. Hence, under conditions of fixed thermal input power, couples containing 3p-PbSnTe would experience (1) a decreasing hot-junction temperature, (2) a constant cold-junction temperature, and (3) a decreasing electrical output power.

In the following discussion, attention is focused on the design and operation of a test apparatus which closely approximates conditions existing in actual thermoelectric generators.

DISCUSSION

Design of Experimental Apparatus

A comprehensive study of life-testing techniques, i.e., the measurement of output power as a function of time, was performed, with particular attention being given to the applicability of the derived

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* Eggers, P. E., et al., "An Advanced Thermoelectric Life Test and Evaluation Study", Final Report, Contract NAS5-10497 (September 28, 1968).

life-test data to the prediction of RTG performance. The results of this study revealed that, in general, the acquisition of meaningful life-test data cannot be achieved within the framework of conventional life-testing techniques, viz., testing under conditions of constant hot- and cold-junction temperatures and unknown thermal input power. Likewise, a study of efficiency-measurement techniques, i.e., the measurement of the ratio of electrical output power to the thermal input power, was performed with particular attention being given to maximizing the accuracy of the measurement while minimizing the complexity of the technique. The results of this study revealed that the electrical output power of thermoelectric couples operating at fixed cold- and hot-junction temperatures will increase with increasing parasitic heat losses from the periphery of the thermoelectric couples, and these losses should, therefore, be minimized. The increase in the electrical output power is the result of a decrease in the internal resistance caused by parasitic heat-loss-induced changes in the temperature distribution along the length of the thermoelectric couple. Hence, minimizing parasitic thermal losses not only permits operation of tests under conditions of constant thermal input power but also provides measured output power values which are realistic in terms of actual generator performance.

Thermal Insulation

The performance of life tests under conditions of constant thermal input power requires a thermal insulation and thermal guarding system (optional) which can maintain parasitic thermal losses from the heat source (electrical heater) below 10 to 15 percent of the total input power. This requirement is particularly demanding since certain life tests are conducted at hot-junction temperatures in excess of 900 C. In conventional life-test apparatus, parasitic losses usually exceed 90 percent of the thermal input power and, hence, any attempt to regulate the input electrical power to the heater is offset by slight changes in the thermal conductance of the thermal insulation system.

A two-dimensional heat-transfer analysis was performed and revealed that the desired thermal insulation capability could be achieved by performing the tests in a vacuum of $\sim 10^{-4}$ torr together with the use of (1) thermal guard heaters fabricated by winding platinum wire (24 gage) on a ZrO_2 tube, (2) multilayered tantalum foil (2 mils thick) in the temperature range 1200 C to $\sim$700 C, (3) multilayered Stainless Steel 347 foil (2 mils thick) in the temperature range below $\sim$700 C, and (4) ZrO_2 powder (1-2 μ diameter) in the cavity between the heat-source - thermoelectric couple - heat-sink assembly and the ZrO_2 guard assembly (see Figure 1). The calculated heat losses for a thermal insulation system of this design are (1) $\sim$0.3 watt(th) from the thermoelectric couple (1.5 to 2.0 percent of the total heat flow through the couple) and (2) $\sim$2 watts(th) loss from the heater ($\sim$10 percent of the total heat supplied) based on a temperature distribution mismatch between the thermal guard and the heat-source - thermoelectric couple - heat-sink assembly of $<$50 C.

An alternate approach to the achievement of these low levels of parasitic heat losses involves the use of thin titanium foils ($\sim$12.5 μm) separated by alternate layers (2.5 μm) of ZrO_2. This design* features (1) a high foil density ($\sim$100 layers of foil per 0.25-cm thickness), (2) low-conduction heat transfer from the hot zone in the longitudinal direction as a result of the use of thin, low thermal conductivity metals, and (3) sufficiently low thermal conductivity to eliminate the need for an

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* Commercially available from Thermo Electron Corporation, Waltham, Massachusetts.

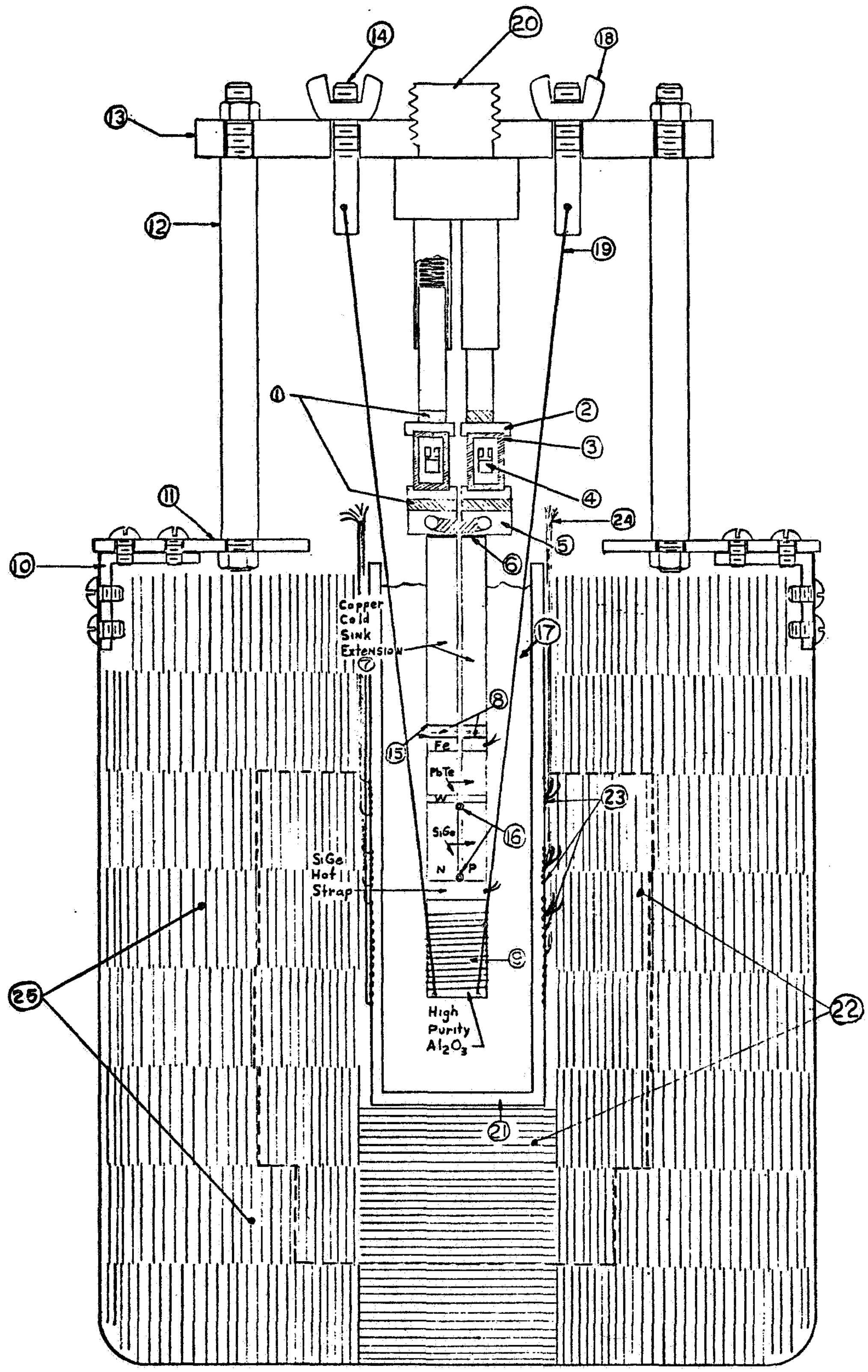


FIGURE 1. LIFE-TEST EFFICIENCY APPARATUS
(Bell-jar enclosure not shown)

Legend (Figure 1)

Item	Description
1	Epoxy bonds
2	Copper load cell platen
3	Aluminum load cell base
4	Strain gauge, Micromeasurements, Gauge Type EP-08-125AD-120
5	Water-cooled heat sinks
6	Pb-Sn solder joint
7	Copper cold sinks
8	Copper-Constantan thermal flux transducers
9	Al_2O_3 heater base - platinum heater element
10	Angular brackets
11	Upper ring
12	Support studs
13	Load ring
14	Wire supports
15	In-Sn solder joints
16	Alumina thermocouple holders
17	Thermal insulating powder (ZrO_2)
18	Wing nuts
19	TZM wire
20	Spring load assembly
21	1-3/4" OD x 1/8" wall, zirconia tube
22	Tantalum (high-temperature region) multifoil thermal insulation
23	Platinum heating element wires (thermal guards)
24	Platinum thermocouples
25	Stainless Steel 347 (low-temperature region) multifoil thermal insulation

electrically heated thermal guarding system. The longitudinal conduction heat transfer through a thermal insulation of this design can be further reduced by decreasing the number of foils used from $\sim$100 in the heater zone to $\sim$20 in the low-temperature region of the thermal insulation as shown in Figure 2.

Heat Source

A capability for long-term testing at hot-junction temperatures up to 1000 C, i.e., heater-element temperatures of up to 1200 C, was accomplished by use of a resistance heater consisting of platinum wire (24 gage) wound on a high-purity Al_2O_3 cylinder (McDanel AP-35). Dual windings were used in order that the countercurrent flow in each winding would serve to minimize magnetic-field-induced effects in the thermoelectric couple when the heater is used in conjunction with a d-c power supply. The heat-source - thermoelectric couple - heat-sink assembly was suspended from the heat-sink support using molybdenum alloy wires (TZM alloy) (as shown in Figure 1) in order to (1) minimize heat losses and (2) facilitate the positioning of the entire assembly inside the ZrO_2 thermal guard cavity.

Heat Sink

The heat-sink assembly contains (1) heat-flux transducers for monitoring heat flow through each leg of the thermoelectric couple, (2) load cells for monitoring spring-loading pressure applied throughout the test, and (3) water-cooled copper heat sink for controlling the cold-

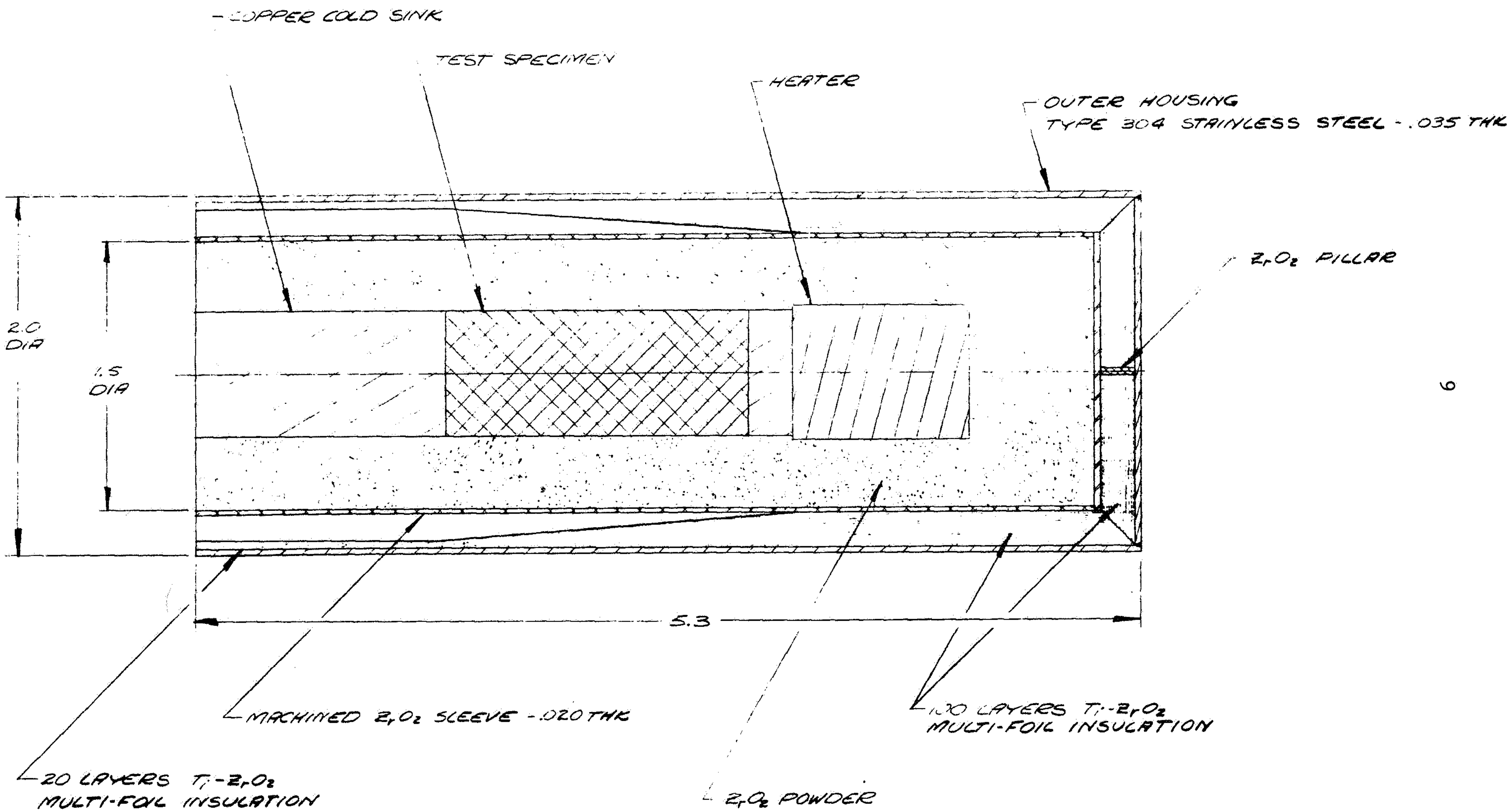


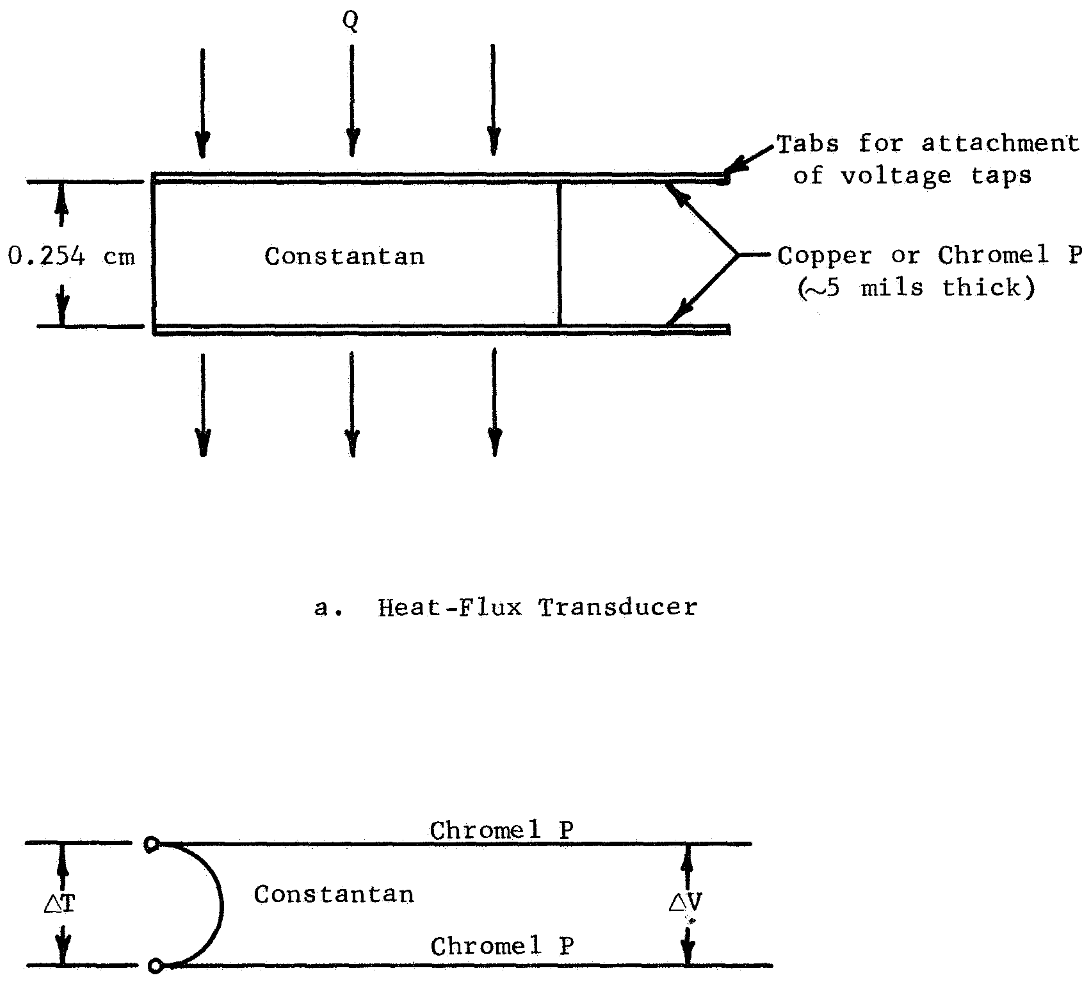
FIGURE 2. MULTIFOIL THERMAL INSULATION

junction temperature of the thermoelectric couple. The heat-flux transducers (supplied by Heat Technology Laboratories) were fabricated by metallurgically bonding copper foil (low-temperature applications) or Chromel P foil (high-temperature applications) to a 0.254-cm-thick layer of Constantan. Operation of this transducer is based on the principle of the differential thermocouple and the output voltage is approximately linear with respect to the thermal flux, i.e., the temperature difference imposed between the thermocouple junctions formed at either side of the transducer (see Figure 3). These transducers have been individually calibrated and feature a sensitivity of $\sim 40\ \mu v/\mathrm{watt(th)/cm}^2$ and are accurate to within 5 percent.

Calibration Procedure

The heat-flux transducers and the thermal insulation system were qualified by a calibration procedure involving the use of a Pyroceram 9606* "standard" whose thermal conductivity closely matches that of typical thermoelectric materials. In addition, a second heat-flux transducer is used at the hot side of the Pyroceram 9606 specimen in order to monitor heat input as well as the heat output measured by the transducers at the cold end of the specimen (see Figure 4). A comparison of the measured heat input and output of the Pyroceram 9606 specimen yields the net heat loss from the specimen. This measured loss, when applied as a correction to the calculated heat flow through the Pyroceram 9606 specimen (based on the measured temperature difference

* Robinson, H. E., et al., "The Current Status of Thermal Conductivity Reference Standards at the National Bureau of Standards", NBS Report Number 8300 (March, 1964).



a. Heat-Flux Transducer

b. Analogue Thermocouple Circuit

FIGURE 3. HEAT-FLUX TRANSDUCER

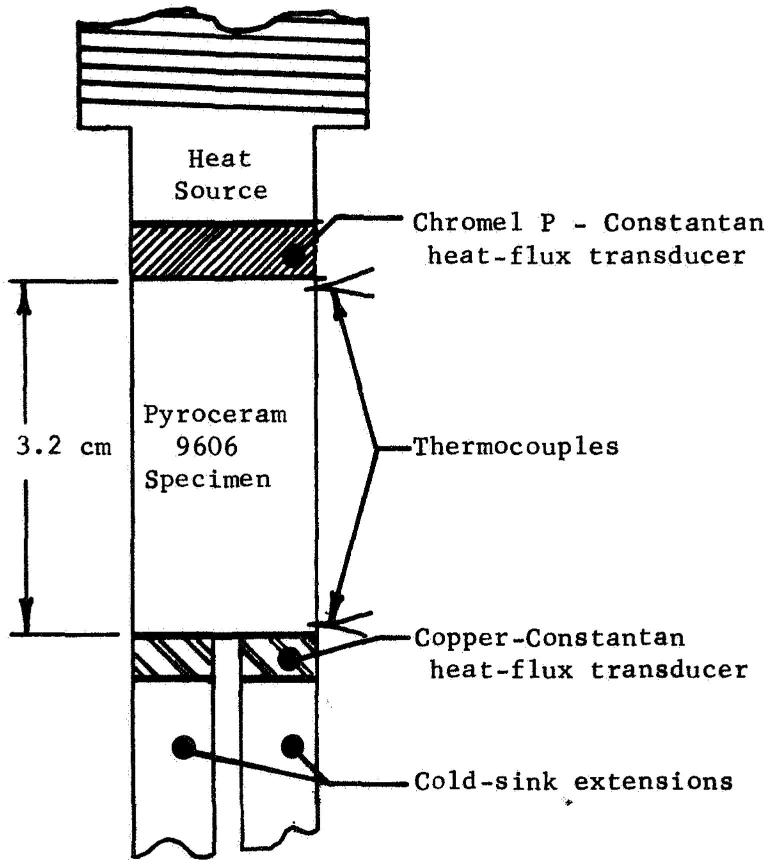


FIGURE 4. CALIBRATION STANDARD

across the Pyroceram 9606 specimen and its known thermal conductivity), provides a means for calibrating the heat-flux transducers at the cold side of the specimen. This calibration procedure is used throughout the range of hot- and cold-junction temperatures associated with the thermoelectric couple tests.

Fabrication of Segmented Couples

A total of four segmented couples containing SiGe and PbTe segments were fabricated for performance testing. The SiGe segments were bonded into a "U-shaped" couple with a p-type SiGe hot strap and tungsten shoes (see Figure 5). The PbTe segments were prepared as separate units for operation in pressure contact to the tungsten shoes of the SiGe couple.

The SiGe components and tungsten shoes were bonded into a couple by means of gold as a brazing agent. The brazing was accomplished using technology developed in earlier segmenting studies*. The gold was incorporated in the junctions in the form of foil. The assembled components were held in a differential thermal expansion bonding fixture and were brazed in vacuum for 1/2 hr at 1066 C (1950 F).

The PbTe segments were made by pressing PbTe powder and the cold-junction shoe into a composite body followed by sintering in hydrogen at 649 C (1200 F) for 1 hr under 100-psi spring loading. The n-type element was made with iron shoes bonded directly to the PbTe. The p-type element

* Kortier, W. E., Mueller, J. J., Freas, D. G., and Eggers, P. E., "A Research and Development Program for Segmenting SiGe and PbTe Thermoelectric Materials", NAS5-10185, Final Summary Report dated December 15, 1966.

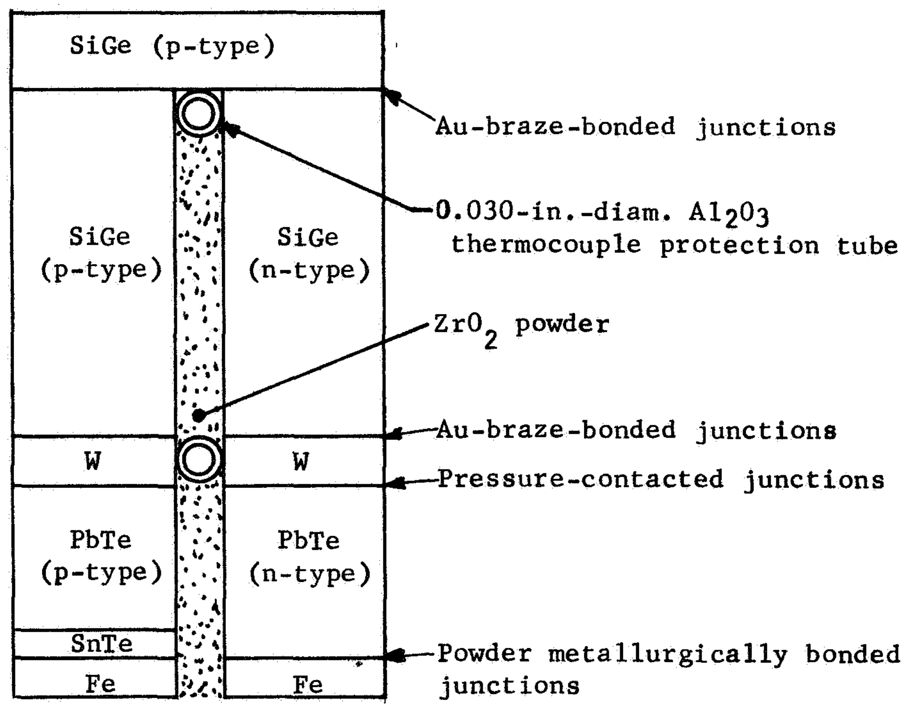


FIGURE 5. SEGMENTED COUPLE FOR PERFORMANCE TESTING

was made with a 1/32-in.-thick layer of tin telluride (SnTe) between the PbTe and iron shoe. The SnTe has been found to yield a stronger bonded element with lower effective contact resistivity than obtainable with iron bonded directly to the 2p-PbTe.

Experimental Results

A detailed description of the measurement procedure as well as the supporting equipment required for these measurements appears in Appendix A.

Energy-conversion-efficiency measurements were successfully completed on two of the four SiGe-PbTe segmented couples. The SiGe hot straps on the remaining two segmented couples fractured during installation into the test apparatus. The couple configuration (see Figure 5) used for these tests was selected based on its high-temperature capability (927 C) and its potential for high-energy-conversion efficiency ($\sim$10 percent). The energy-conversion-efficiency measurements were performed at a nominal hot-junction and cold-junction temperature of 927 and 50 C, respectively. The results of these measurements are summarized in Table 1.

The deficiency in the observed operating current, I, and conversion efficiency, $\eta_{T/E}$, may be the result of excessive electrical contact resistance at the PbTe-W pressure-contacted junction (see Figure 5). Previous experimental studies have indicated that the PbTe-W pressure-contacted junction has an electrical contact resistivity of only 200 to 300 $\mu\Omega\text{-cm}^2$ at 800 K. However, improper alignment or inadequate flatness of the adjacent

TABLE 1. CALCULATED AND MEASURED PARAMETERS FOR THE SiGe-PbTe SEGMENTED COUPLE

Parameter	Theoretical	Experimental[a] Couple No. PG-69-3	Couple No. PG-69-4
T_C (K)	350	325	330
T_I (K)	800	820	830
T_H (K)	1200	1199	1198
A_P (cm^2)	0.578	0.576	0.578
A_N (cm^2)	0.657	0.653	0.656
L_P (SiGe) (cm)	2.04	2.04	2.01
L_P (PbTe) (cm)	0.80	0.79	0.77
L_N (SiGe) (cm)	2.02	2.03	1.99
L_N (PbTe) (cm)	0.87	0.87	0.87
Thickness (hot strap) (cm)	0.64	0.63	0.64
Spring-loading pressure (psi)	120	125	125
I[b] (amp)	7.0	5.9	6.1
P[b] (watts(e))	1.250	1.27[c]	1.30[c]
$\eta_{T/E}$[b] (percent)	10.9	9.8 ± 0.7	9.4 ± 0.7

(a) Hot straps of Couple Numbers PG-69-1 and PG-69-2 were broken during installation of couples into test apparatus.

(b) Parameters measured after ~100 hr at temperature.

(c) Corrected output power to account for Joulean power dissipation in high-resistance SiGe hot strap.

(d) See Appendix B for details of error analysis.

W and PbTe surfaces can cause high contact resistances and, hence, may account for the low value of efficiency observed for the SiGe-PbTe thermoelectric couples. Posttest examination of the pressure-contacted junctions of these couples supports this explanation since there was evidence of only partial contact between the adjacent tungsten and the n-type PbTe surfaces.

CONCLUSIONS AND RECOMMENDATIONS

The experimental results indicate that the life-test - efficiency apparatus described in the preceding discussion performed adequately at heater temperatures up to 1200 C. The technique used for the suspension of the heat-source - thermoelectric couple - heat-sink subassembly permitted convenient installation and removal of test specimens while minimizing the conduction heat losses from the base of the heat source. The thermal insulation system also performed adequately with only 14 to 18 percent of the heat supplied to the heater being lost through the thermal insulation. Based on the low level of parasitic heat loss from the heater, the apparatus should function satisfactorily in the evaluation of thermoelectric performance under conditions similar to actual radioisotope-fueled generator operation, viz., a nearly constant thermal power input to the thermoelectric couples as a function of time.

The close correlation between calculated and experimentally derived performance for the SiGe-PbTe segmented couple further supports the adequacy of this present design for use in the measurement of energy-conversion efficiency.

It is recommended that future efficiency measurements performed on couples containing SiGe include the use of low-resistance hot-strap materials (e.g., $MoSi_2$) since $\sim$10 percent of the total electrical output power of the segmented couples used in these measurements was dissipated in the p-type SiGe hot strap. In addition, life testing should be performed in the present apparatus at typical operating temperatures in order to qualify the long-term stability of the apparatus, particularly, the thermal insulation system. Finally, it is recommended that a passive thermal insulation system be used (see Figure 2) in order to simplify the measurement apparatus and maximize the precision of measurement apparatus.

ACKNOWLEDGMENTS

Grateful acknowledgments are due to W. E. Kortier and M. Pobereskin of Battelle-Columbus for their technical review of this work and also M. L. Paquin of Thermo Electron Corporation for his assistance in the design of the passive thermal insulation system.

APPENDIX A

<u>RECOMMENDED PRACTICE FOR PERFORMING LIFE TESTS AND EFFICIENCY MEASUREMENTS FOR THERMOELECTRIC COUPLES</u>

APPENDIX A

RECOMMENDED PRACTICE FOR PERFORMING LIFE TESTS AND EFFICIENCY MEASUREMENTS FOR THERMOELECTRIC COUPLES

1. SCOPE

1.1 This method of measurement provides a procedure for determining the electrical output power and energy-conversion efficiency of thermoelectric couples as a function of time under conditions of constant or controlled thermal input power. The measurement technique features a single instrument accuracy of ±7 percent for couples operating between cold-junction temperatures as low as 50 C and hot-junction temperatures as high as 1000 C.

1.2 Procedures are outlined for the calibration of the life-test - efficiency measurement-measuring apparatus.

2. SUMMARY OF METHOD

2.1 In this method, the life testing is performed by maintaining the thermal input power supplied to the thermoelectric couple constant and monitoring the couple's hot- and cold-junction temperatures, open- and closed-circuit voltage, and operating current as a function of time. The couple output power stability under conditions of constant thermal input power can, thus, be determined from these measurements. Similarly, the energy-conversion efficiency can be determined by measuring the thermal power flowing through the thermoelectric couple as well as the electrical output power of the couple.

2.2 The couple output power is obtained from the product of the operating current, I, and the closed-circuit voltage, V_{cc}, of the couple.

2.3 The external load for the life testing must be established initially and maintained <u>constant</u> throughout the test period.

3. APPARATUS

A diagram of the measurement apparatus is shown in Figure A-1.

3.1 Specimen Preparation - The surface of the couple shall be free from visible defects such as cracks, pits, blisters, and gross surface oxide. Pressure-contacted junctions shall be assembled with the adjacent surfaces in intimate contact in order to insure sufficiently low electrical contact resistivity during the test.

3.2 Specimen Supports - The thermoelectric couple shall be supported between the platinum-wound, high-purity Al_2O_3 heater and the heat-flux transducers (see Figure A-1). The use of high-purity Al_2O_3 (McDanel AP-35) at the hot-junction support insures a high degree of electrical isolation at elevated temperatures (~1000 C) as well as being chemically inert with respect to thermoelectric materials, e.g., SiGe.

3.3 Temperature Measurement - A temperature-measuring thermocouple such as platinum versus platinum-rhodium shall be encased in high-purity Al_2O_3 protection tubes and positioned adjacent to the junction of interest as shown in Figure A-1. Preferably, the thermocouple shall be attached directly to the couple. However, the direct contact of the thermocouples with the thermoelectric specimen shall include only the use of materials which are known to be chemically compatible with the specimen at the operating temperatures. The thermocouples should be accurate to within ±0.25 percent. Long-term stability of the thermocouples operating at elevated temperatures may be improved by using platinum - 6 percent rhodium versus platinum - 30 percent rhodium since the resulting diffusion of rhodium from the thermocouple leg of higher concentration into the leg of lower concentration will have a less pronounced effect on the thermocouple emf of this particular thermocouple than in the case of thermocouples containing unalloyed legs, e.g., "pure" platinum versus platinum - 10 percent rhodium.

3.4 Thermal Power Control and Measurement

3.4.1 Suitable means shall be provided for maintaining the thermal input power to the thermoelectric couple constant during the period of the life test. This can be readily accomplished using a regulated d-c power supply (nominally <0.05 percent line and load regulation). The thermal power flow through the couple can be accurately measured by positioning heat-flux transducers at the cold junction of each leg of the thermoelectric couple (see Figure A-1). The transducers used in the measurement of heat flux shall be precalibrated* over the temperature range of interest and shall be accurate to within ±5 percent.

3.4.2 The measured heat flux shall be used in conjunction with the measured electrical output power to calculate the energy-conversion efficiency of the thermoelectric couple, i.e., the ratio of the electric output power and the thermal input power of the couple.

3.5 Heat-Sink Temperature Control - Suitable means shall be provided for maintaining the thermoelectric couple cold-junction temperature constant (within ±1.0 C) during the period of the life test. This constraint is necessary for the simulation of actual conditions present in thermoelectric generators containing heat sources of constant thermal inventory. This may be accomplished by use of water-cooled heat sinks at the extreme end of each leg of the specimen and the water temperature may be maintained nearly constant by use of a water-temperature controller.

3.6 Load-Cell Subassemblies - Load cells shall be attached to the supports for both legs of the thermoelectric couple (see Figure A-1) and shall have a sensitivity of at least 3 psi/division as measured on strain-gage potentiometers.

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* Supplied by Heat Technology Laboratories, Huntsville, Alabama.

The measurement of the spring-load pressure applied to each leg of the thermoelectric couple shall be monitored during the period of the life test in order to detect any changes in the applied pressure and, thus, facilitate the diagnosis of the cause of any degradation in electrical output power of the thermoelectric couple.

3.7 Heat Source - The heat source shall be designed to provide a long-term (>10,000 hr) testing capability while operating in vacuum ($<10^{-4}$ torr) at temperatures up to 1500 K (2240 F). This capability may be achieved by use of a resistance heater consisting of platinum wire (24 gage) wound on a high-purity alumina cylinder (McDanel AP-35). Dual windings shall be used in order that the countercurrent flow in each winding will serve to minimize magnetic-field-induced effects in the thermoelectric couple. This precaution is necessary when the heater is used in conjunction with a d-c power supply.

3.8 Thermal Insulation - The thermal insulation and optional thermal guarding system shall be capable of limiting parasitic heat losses from the specimen heat source (see Figure A-1) to less than 15 percent of the total input power. This capability may be achieved by operating the thermal insulation in a vacuum of $<10^{-4}$ torr together with the use of (1) thermal guard heaters fabricated by winding platinum wire (24 gage) on a ZrO_2 tube, (2) multilayered tantalum foil (2 mils thick) in the temperature range 1200 C to ~700 C, (3) multilayered Stainless Steel 347 foil (2 mils thick) in the temperature range below ~700 C, and (4) ZrO_2 powder (1-2 μ diameter) in the cavity between the heat-source - thermoelectric couple - heat-sink assembly and the ZrO_2 guard assembly. The multilayered foil insulation shall be assembled in 1- to 2-cm-high stages (see Figure A-1) in order to minimize conduction heat transfer from the hot zone in the longitudinal direction.

An alternate approach to the achievement of these low levels of parasitic heat losses involves the use of thin titanium foils ($\sim$12.5 μm) separated by alternate layers (2.5 μm) of ZrO_2. This design* features (1) a high foil density ($\sim$100 layers of foil per 0.25-cm thickness), (2) low-conduction heat transfer from the hot zone in the longitudinal direction as a result of the use of thin, low thermal conductivity metals, and (3) sufficiently low thermal conductivity to eliminate the need for an electrically heated thermal guarding system. The longitudinal conduction heat transfer through a thermal insulation of this design can be further reduced by decreasing the number of foils used from $\sim$100 in the heater zone to $\sim$40 in the low-temperature region of the thermal insulation as shown in Figure A-2.

3.9 Electrical Measuring Apparatus - The recommended circuit to be used for this measurement is shown in Figure A-3 and consists of the following:

3.9.1 Regulated d-c power supply capable of maintaining the power input to the specimen heat source constant to within 0.1 percent.

3.9.2 The measurement of (1) the specimen hot-, intermediate-, and cold-junction temperatures, (2) the heat-source and guard-ring (optional) temperatures, (3) the open- and closed-circuit voltage of the specimen, (4) the voltage drop across the standard resistor, and (5) the voltage drop across the heat-flux transducers shall be performed using an integrating digital voltmeter (or a comparable measuring instrument) in conjunction with a line conditioner having a response time of 25 to 50 microseconds which minimizes the effects of high-speed line transients during the measurement of low-level d-c voltages. This d-c-measuring instrument should have microvolt resolution and be accurate to within ±6 μvolts over the entire range of measurement or

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* Commercially available from Thermo Electron Corporation, Waltham, Massachusetts.

±(0.01 percent of reading + 0.005 percent of full scale). If a digital voltmeter is used, the effective noise-rejection capability of the voltmeter should be at least 120 to 140 db and a common mode rejection of 120 db or more. The integrating capability of the specified digital voltmeter (see Figure A-3) reduces superimposed noise by averaging out the random signal.

3.9.3 A multipole potential selector switch shall be used to monitor the voltage drops across the thermocouples, heat-flux transducers, standard resistor, and the specimen.

3.10 Hermetically Sealed Enclosure - The test apparatus (see Figure A-1) shall be contained in a hermetically sealed enclosure (e.g., bell-jar cover with O-ring seal on base plate) with a total leak rate of $<1 \times 10^{-8}$ atm-cc/sec as determined by a calibrated helium leak detector.

3.11 Materials Selection - The test apparatus shall be constructed using only low-vapor-pressure, low-porosity materials in order to avoid contamination of the specimen with volatiles or entrapped gases (air). The direct contact of the supports, voltage probes, and thermocouples with the thermoelectric specimen shall include only the use of materials which are known to be chemically compatible with the specimen.

4. MEASUREMENT PROCEDURE

4.1 The thermoelectric couple shall be examined prior to installation into the test apparatus to insure that it is free of gross surface oxide and imperfections such as blisters or pits which might interfere with the performance of the couple. In addition, the adjacent surfaces associated with pressure-contact junctions shall be planar and in close contact to insure low electrical contact resistivity.

4.2 The thermoelectric couple shall be positioned between the two supports with an applied spring-loading pressure of 100 psi in order to insure good electrical contact at pressure-contact junctions as well as to insure good thermal contact at the specimen - support interface (see Figure A-1).

4.3 Insert heat-source - thermoelectric couple - heat-sink subassembly (see Figure A-1) into ZrO_2 cavity and position subassembly such that a gap of >1.0 cm exists between the base of the heat source and the base of the ZrO_2 cavity. The open regions of the cavity surrounding the inserted subassembly are next filled with dry, high-purity ZrO_2 powder (1 to 2 μ diameter powder). This low thermal conductivity powder serves to minimize parasitic heat losses from the heat-source - thermoelectric couple - heat-sink subassembly as well as suppressing sublimation which might otherwise occur in some thermoelectric materials, e.g., PbTe.

4.4 Insert the thermoelectric couple and its supporting test fixture into the gas-tight enclosure (specified in Section 3.6). The enclosure shall be evacuated to $\sim 10^{-4}$ torr, backfilled with inert gas (e.g., argon), and reevacuated to $\sim 10^{-4}$ torr. This purging procedure shall be repeated several times at room temperature and again with the heater operating at $\sim$300 C to facilitate outgassing of the apparatus, particularly the region filled with the ZrO_2 powder. Finally, the system shall be evacuated to $<10^{-4}$ torr and maintained at or below this vacuum level throughout the duration of the test.

4.5 The current leads from the heater shall be attached to a suitable regulated power supply. The power input to the heater shall be adjusted in order to achieve the desired thermal gradient along the thermoelectric couple. The guard heaters (optional) shall be adjusted in order to maintain the temperature profile of the guard-heater subassembly within 25 to 50 C of the temperature profile of the thermoelectric couple. This "matching" of guard heaters to thermoelectric couple can be achieved by attaching thermocouples to the guard-heater subassembly and positioning them in the plane which (1) intersects the heater thermocouple and hot-, intermediate-, and cold-junction thermocouples and (2) is perpendicular to the longitudinal axis of the thermoelectric specimen (see Figure A-1).

4.6 All thermocouples shall be attached to appropriate compensating lead wires. Care should be taken to avoid (in the evacuated region) the use of wiring insulated by polyethylene, polyvinyl chloride, or other high-vapor-pressure materials.

4.7 The specimen should remain at temperature for ~100 hr before initiating the life test or efficiency measurements in order to establish equilibrium conditions within the junctions of the thermoelectric couple, particularly in the case of pressure-contacted junctions.

4.8 Having reached equilibrium conditions, the voltages associated with the thermocouples, heat-flux transducers, standard resistor, and the thermoelectric couple are measured. The electrical output power and energy-conversion efficiency of the thermoelectric couple shall be computed according to the following relation:

$$P(t)^{*} = \frac{V_s(t)}{R_s} \cdot V_{cc}(t) \quad ,$$

$$\eta_{T/E}(t) = \frac{P(t)}{(Q_n(t) + Q_p(t))} \cdot 100 \quad ,$$

* Note that the relations, V^2_{cc}/R_{int} or $V^2_{oc}/(4 \cdot R_{int})$, should not be used for computing the output power since the operating current or external load yielding maximum conversion efficiency are not necessarily coincident with that yielding maximum output power.

where:

$P(t)$ = electrical output power (in watts(e)) of thermoelectric couple at time, t

$V_s(t)$ = potential difference (in volts) across standard resistor at time, t

$V_{cc}(t)$ = potential difference (in volts) across thermoelectric couple under closed-circuit conditions at time, t

R_s = resistance of standard resistor (in ohms)

$\eta_{T/E}(t)$ = energy-conversion efficiency (in percent) of thermoelectric couple at time, t

$Q_n(t)$, $Q_p(t)$ = heat transferred (in watts(th)) through n-leg and p-leg, respectively, at time, t.

4.9 The external load resistance of the thermoelectric couple (see Figure A-3) shall be adjusted in order to achieve the desired couple-operating condition, e.g., maximum initial electrical output power, maximum initial energy-conversion efficiency, or projected maximum power or conversion efficiency at "end of life". No further adjustments shall be made once the external resistance is established except for the optional "mapping" of the couple performance as a function of external load resistance at end-of-life conditions.

5. CALIBRATION

The heat-flux transducers and the thermal insulation system shall be qualified by a calibration procedure involving the use of a Pyroceram 9606 "standard" or any other suitable thermal conductivity standard whose thermal conductivity closely matches that of the thermoelectric materials being tested. In this calibration procedure, a second heat-flux transducer is used at the hot side of the "standard" specimen in order to monitor heat input as well as the heat output measured by the transducers at the cold end of the specimen (see Figure A-1). A comparison of the measured heat input and output of the standard specimen yields the net heat loss from the specimen. This measured loss, when applied as a correction to the calculated heat flow through the standard specimen (based on the measured temperature difference across the standard specimen and its known thermal conductivity), provides a means for calibrating the heat-flux transducers at the cold side of the specimen. This calibration procedure shall be used through the range of the hot- and cold-junction temperatures associated with the thermoelectric couple tests.

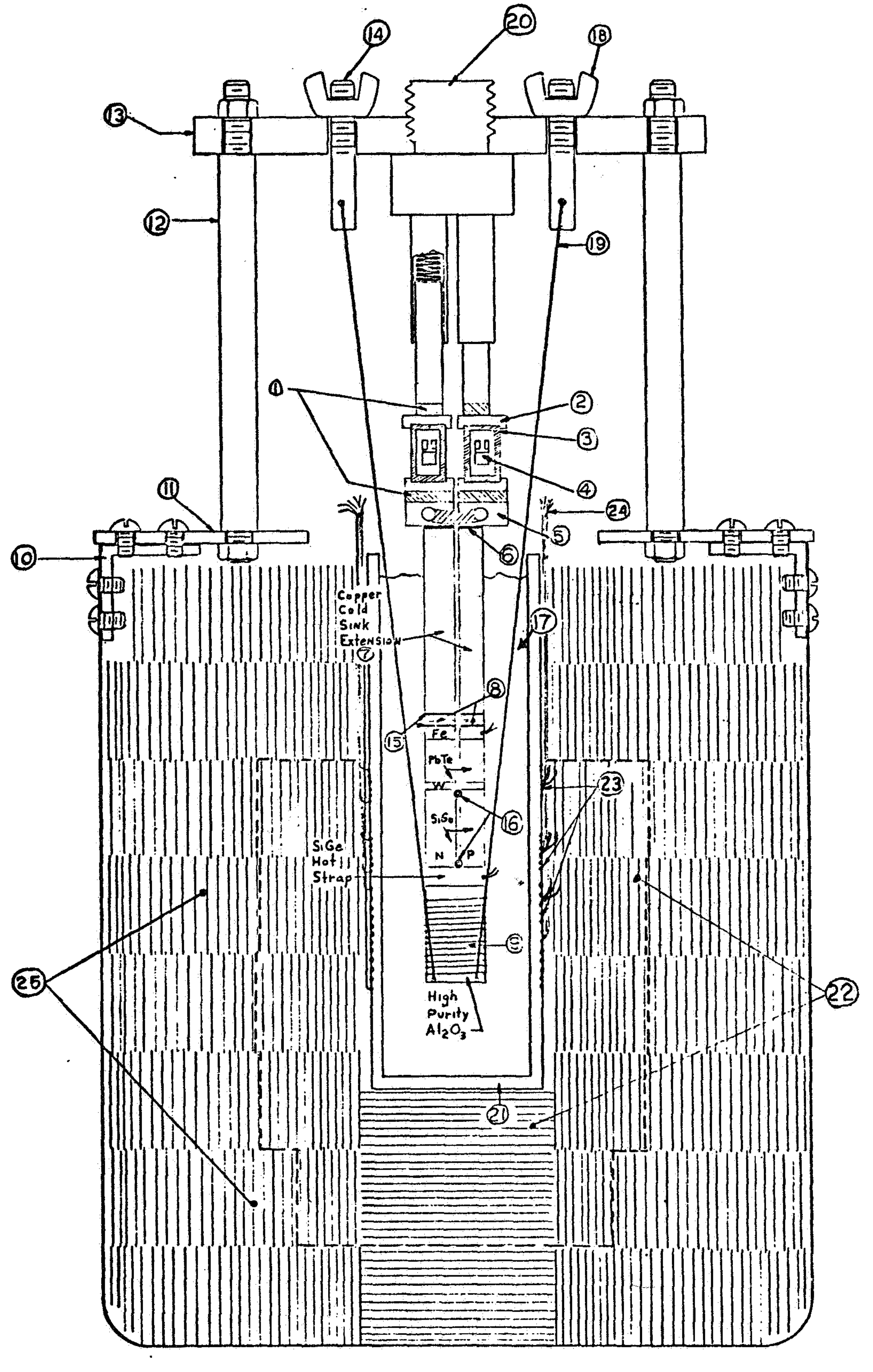


FIGURE A-1. LIFE-TEST EFFICIENCY APPARATUS
(Bell-jar enclosure not shown)

Legend (Figure A-1)

Item	Description
1	Epoxy bonds
2	Copper load cell platen
3	Aluminum load cell base
4	Strain gauge, Micromeasurements, Gauge Type EP-08-125AD-120
5	Water-cooled heat sinks
6	Pb-Sn solder joint
7	Copper cold sinks
8	Copper-Constantan thermal flux transducers
9	Al_2O_3 heater base - platinum heater element
10	Angular brackets
11	Upper ring
12	Support studs
13	Load ring
14	Wire supports
15	In-Sn solder joints
16	Alumina thermocouple holders
17	Thermal insulating powder (ZrO_2)
18	Wing nuts
19	TZM wire
20	Spring load assembly
21	1-3/4" OD x 1/8" wall, zirconia tube
22	Tantalum (high-temperature region) multifoil thermal insulation
23	Platinum heating element wires (thermal guards)
24	Platinum thermocouples
25	Stainless Steel 347 (low-temperature region) multifoil thermal insulation

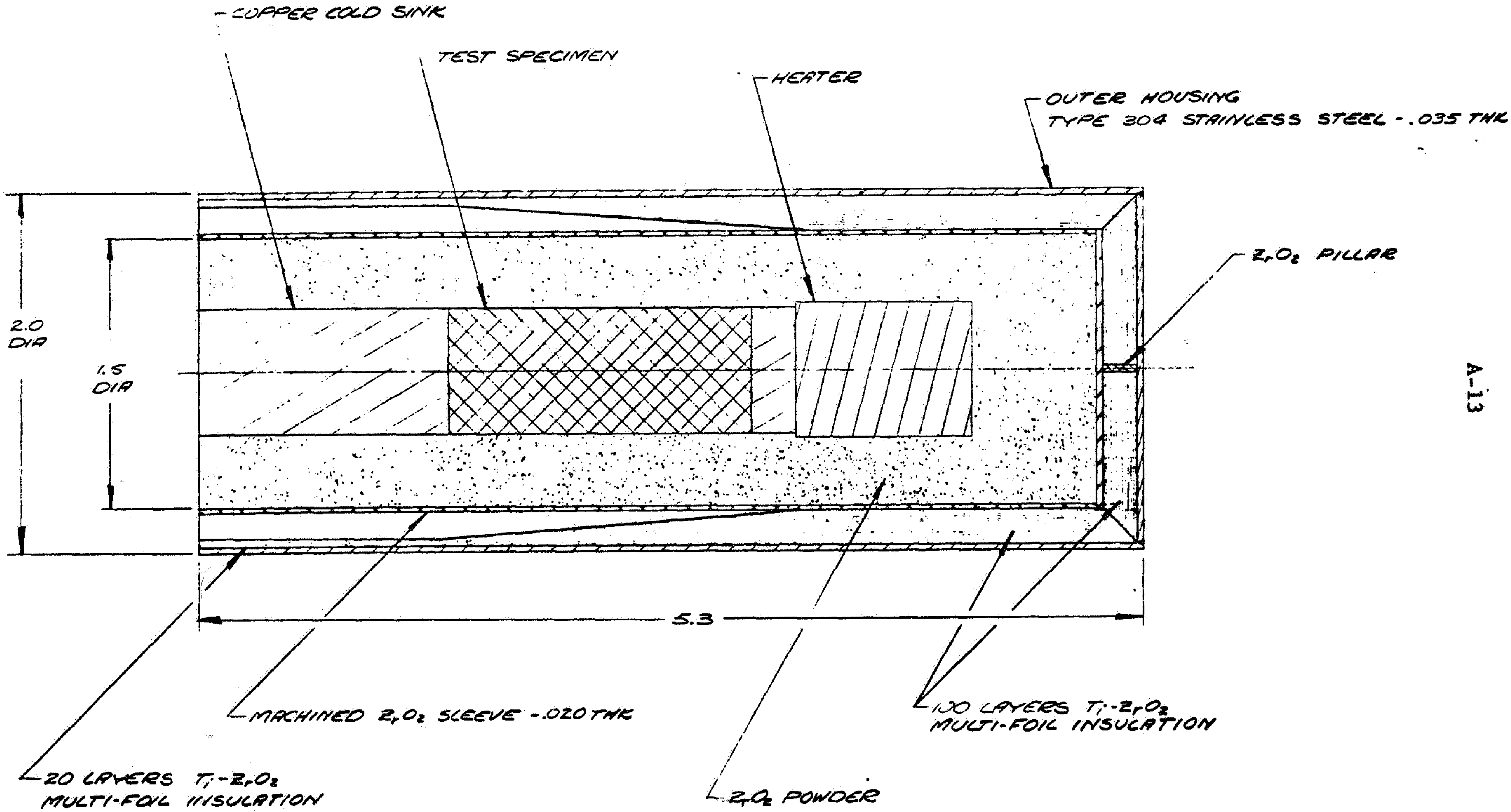
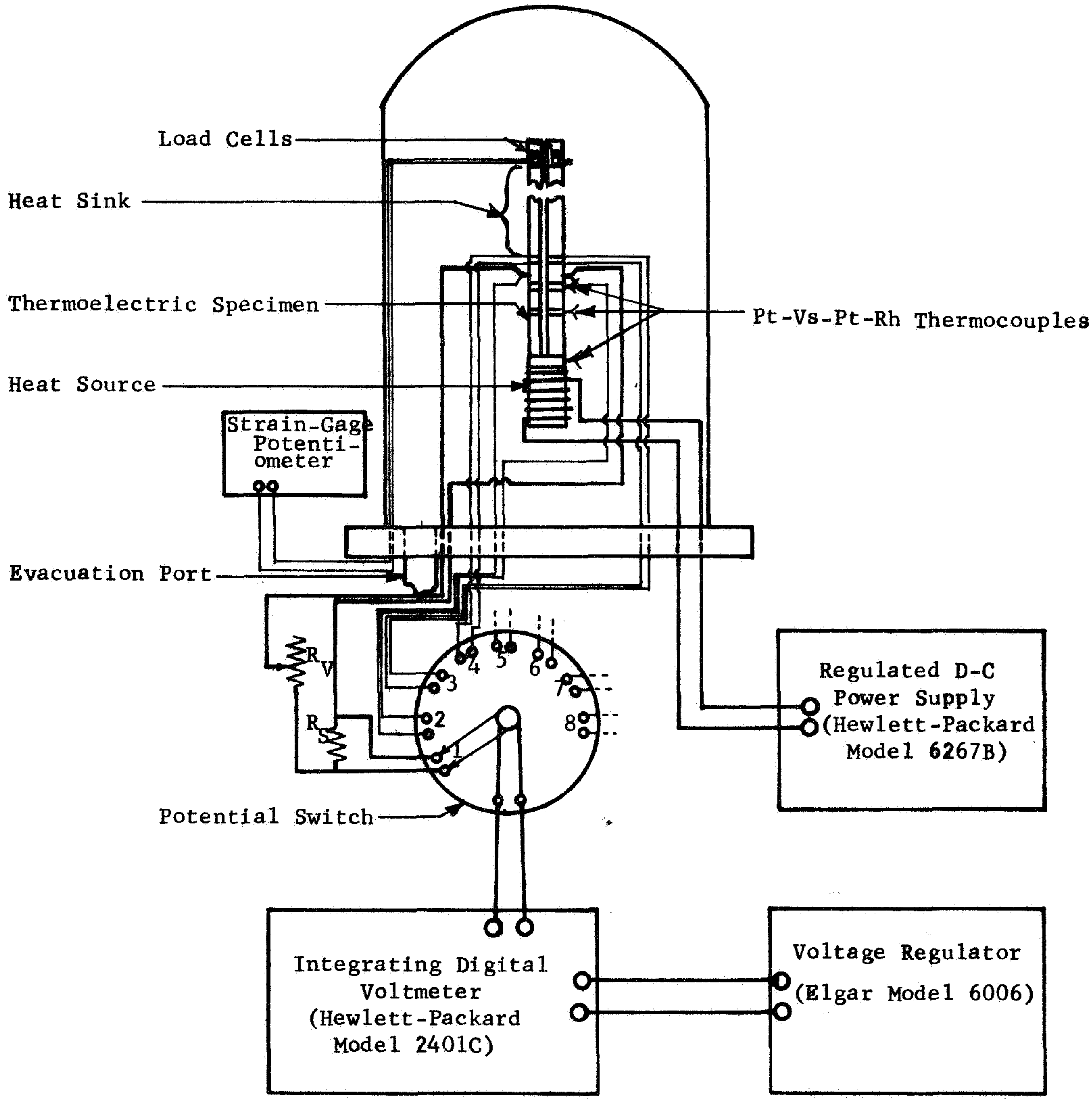


FIGURE A-2. MULTIFOIL THERMAL INSULATION



1 - Voltage drop across standard resistor
2 - Voltage drop across specimen
3,4 - Voltage drops across heat-flux transducers
5-8 - Voltage drops across heater thermocouple and hot-, intermediate, and cold-junction thermocouples (leads not shown)

FIGURE A-3. SCHEMATIC DIAGRAM OF LIFE-TEST - EFFICIENCY APPARATUS

APPENDIX B

ERROR ANALYSIS OF ENERGY-CONVERSION-EFFICIENCY-MEASUREMENT TECHNIQUE

APPENDIX B

ERROR ANALYSIS OF ENERGY-CONVERSION-EFFICIENCY-MEASUREMENT TECHNIQUE

The uncertainty limits for the energy-conversion-efficiency-measurement technique were calculated using simple differential calculus to identify the variables and their effect upon the total uncertainty of the measurement system. The approach is one of obtaining the total differential of the equation which describes the parameter being investigated.

In the subject case, the equation for η, the energy-conversion efficiency, is expressed in terms of the measured parameters:

$$\eta = [\frac{V_s}{R_s} \cdot V_{cc}]/Q \quad , \tag{1}$$

where:

V_s = potential difference (in volts) across standard resistor

V_{cc} = potential difference (in volts) across thermo-electric couple under closed-circuit conditions

R_s = resistance of standard resistor (in ohms)

Q = heat transferred (in watts(th)) through couple.

Using a technique developed in the literature*, the exact differential for the above equation is:

$$D\eta = \frac{\partial\eta}{\partial V_s} dV_s + \frac{\partial\eta}{\partial V_{cc}} dV_{cc} + \frac{\partial\eta}{\partial R_s} dR_s + \frac{\partial\eta}{\partial Q} dQ \ . \tag{2}$$

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* Baird, D. C., An Introduction to Measurement Theory and Experiment Design, Prentice-Hall, 1962.

Approximating this differential equation with a finite difference equation:

$$\Delta\eta = \frac{\partial\eta}{\partial V_s}\,\delta V_s + \frac{\partial\eta}{\partial V_{cc}}\,\delta V_{cc} + \frac{\partial\eta}{\partial R_s}\,\delta R_s + \frac{\partial\eta}{\partial Q}\,\delta Q \quad , \tag{3}$$

where $\Delta\eta$ represents the plus or minus value of the uncertainty limit assigned to the efficiency value measured. The partial differential equations listed below are obtained by differentiating Equation 1.

$$\frac{\partial\eta}{\partial V_s} = \left(\frac{V_{cc}}{R_s}\right)/Q \ . \tag{4}$$

$$\frac{\partial\eta}{\partial V_{cc}} = \left(\frac{V_s}{R_s}\right)/Q \ . \tag{5}$$

$$\frac{\partial\eta}{\partial R_s} = \left(\frac{V_s \cdot V_{cc}}{R_s^{\,2}}\right)/Q \ . \tag{6}$$

$$\frac{\partial\eta}{\partial Q} = \left(\frac{V_s \cdot V_{cc}}{R_s}\right)/Q^2 \ . \tag{7}$$

Substituting Equations 4 through 7 into Equation 3 yields:

$$\Delta\eta = \left|\left[\left(\frac{V_{cc}}{R_s}\right)/Q\right] \cdot \delta V_s\right| + \left|\left[\left(\frac{V_s}{R_s}\right)/Q\right] \cdot \delta V_{cc}\right| + \left|\left[\left(\frac{V_s \cdot V_{cc}}{R_s^{\,2}}\right)/Q\right] \cdot \delta R_s\right| + \left|\left[\left(\frac{V_s \cdot V_{cc}}{R_s}\right)/Q^2\right] \cdot \delta\right. \tag{8}$$

The δ values are those uncertainty values associated with the measurement apparatus. This uncertainty is derived from digital voltmeter error, standard resistor error, and heat-flow-measurement error. The resultant δ values used in the computation of the uncertainty limits are listed below for each component.

δ Factor Affected	Component
δV_s, δV_{cc}	Voltmeter - ±6 microvolts over full range of measurement
δR_s	Voltmeter and standard resistor - ±0.01 milliohm
δQ	Voltmeter and heat-flux transducer - ±6.5 percent

Factoring the above values into Equation 8 yields an uncertainty limit of ±0.67 in units of "efficiency percent" or ±7.0 percent of the measured efficiency value. This calculation was based on the values of V_s, V_{cc}, R_s, and Q measured in this present study. However, >90 percent of the uncertainty in the measurement is due to that associated with the heat-flow measurement and, hence, the uncertainty in the total measurement can be approximated by the error in the heat-flow measurement alone.