DESIGN AND CONSTRUCTION OF A THERMOELECTRIC COOLING JUNCTION

By

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THERMOELECTRIC COOLING JUNCTION

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PREFACE

During the recent years, as a result of development in semiconductor materials, the science of thermoelectricity has turned into a field of potentially great practical importance. The phenomenon of thermoelectric cooling discovered by Peltier in 1834 continued to be just a matter of academic interest until a few years ago. Now thermoelectric refrigerators and coolers have become a reality in the industry. For some specialized uses these devices have superceded the conventional ones and depending upon the progress in material development are expected to compete with them for the day to day use in foreseeable future.

The purpose of this thesis is to present the design and construction techniques of a single stage thermoelectric cooling device. An experimental cooling junction based on lead telluride elements was constructed in the laboratory. The problems encountered in the construction and the experimental results obtained are also discussed in this thesis.

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CHAPTER I

Introduction

History of Thermoelectric Cooling

The history of thermoelectricity dates back to 1821 when Seebeck (1) observed a thermoelectric current in a closed circuit made up of dissimilar conductors at different junction temperatures. He named this phenomenon "the magnetic polarization of metals and ores produced by a temperature difference." Seebeck did not realize that he had found out a new source of electric current and insisted on interpreting his discovery by the theory that magnetism is caused by temperature difference. However, Seebeck did a lot of experimental work using a great variety of solid and liquid metals, alloys, minerals and semi conductors. He prepared a list of materials in order of the merit of their thermoelectric properties. The accuracy of Seebeck's experiments and thoroughness of his research in this field can be realized from the fact that 125 years later Maria Telkes (2) after surveying all possible materials found that the best couple would be of ZnSb and PbS, which were the first and last members in Seebeck series.

In 1834, Peltier (3) a French watchmaker, observed the phenomenon which is today called "Peltier effect". He observed that when a current is passed through a junction of dissimilar conductor there is absorption or generation of heat depending upon the direction of the current. Peltier, like Seebeck, did not understand the nature of his results. Goldsmid (4) mentions that in 1838 Lenz demonstrated that water could be frozen at a bismuth-antimony junction by passage of current, and on reversing the current, the ice could be melted.

Thomson, later Lord Kelvin (5), in 1854 gave a thermodynamic analysis of thermoelectric effects and established a relationship between Seebeck and Peltier effects. He also discovered a third phenomenon, the "Thomson effect," that of heating or cooling in a homogeneous conductor when an electric current passes in the direction of a temperature gradient. Till the beginning of the twentieth century, no significant progress was made in the science of thermoelectricity. The only devices based on thermoelectricity were thermocouples for measurement of temperature and thermopile for detection of radiant energy.

It was in 1909 and 1911 that Altenkirch (6) first derived satisfactorily the basic theory of thermoelectric generators and refrigerators. He showed that for both applications materials were required with high Seebeck coefficients, high electrical conductivity and low thermal conductivity. Until recently only metals were adopted as thermoelectric elements and no real progress was made. The most widely used device was thermocouple, but in 1930 thermoelectric effects were commercially used in gas appliance burner controls as mentioned by Huck (7).

Advancement in the preparation of semi-conductor materials resulted in renewed interest and progress in the field of thermoelectricity. In 1948 a research group headed by Dr. S. Karrer at Baso Inc. initiated a search for thermoelectric materials having exploitable properties. (7). This research work is being expanded at Minnesota Mining and Manufacturing Company. Several other companies like General

Thermoelectric Corporation, Whirlpool Corporation, General Electric, Westinghouse, etc., are actively busy in research in materials and applications of thermoelectricity. As a result of breakthrough in preparation of materials with desired properties, thermoelectric cooling devices have now become a reality. Several American companies have built heat pump devices ranging from bottle warmers to room air-conditioners. RCA air-conditioned a small room with a thermoelectric device. General Electric and Westinghouse also have produced regrigerators, small room air-conditioners, spot coolers, food cabinets and some other appliances. These are all experimental models. According to Hudelson (8) use of thermoelectric air conditioning equipment has been investigated for application in submarines.

What is the future of thermoelectric devices? There can be no two answers to this question. It will not be long before thermoelectric devices are seen on the market. A detailed market survey recently carried out by Harvard University students (9) indicates that in about five years' time thermoelectric appliances will start competing with the conventional types for specialized uses. According to Ioffe (10) and other Russian workers, it is claimed that Russia is already constructing thermoelectric refrigerators and small air-conditioners on a commercial basis. In the U.S.A., the present material and assembly costs are high but when improved materials are produced in bulk quantities and large scale production methods are adopted for assembly, the cost of thermoelectric devices will definitely come down. Progress in thermoelectric refrigeration and the cost of thermoelectric refrigerators as reviewed by Staebler (11) are shown in Figures 1 and 2. Figure 1 indicates the tremenduous boost thermoelectric applications have received

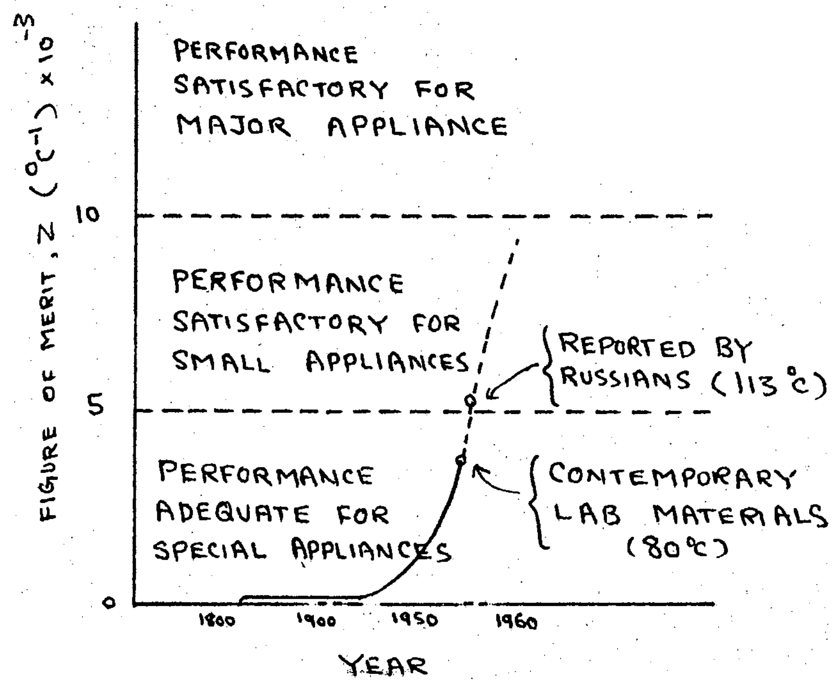


Figure 1. Progress in Thermoelectric Refrigeration

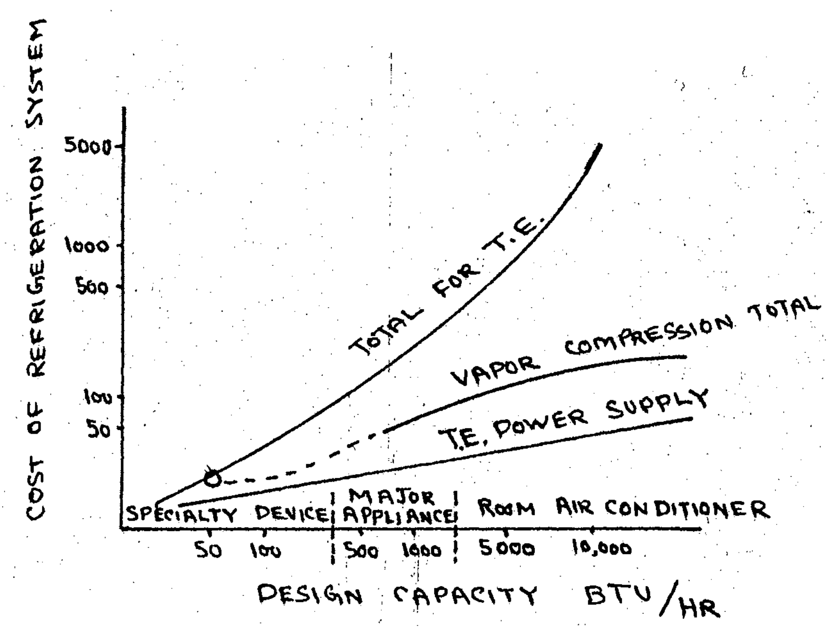


Figure 2. Cost of Thermoelectric Refrigeration

in recent years due to development of suitable material. The material science has just pushed the thermoelectric applications in the range where they may be satisfactory for small appliances. From the point of view of cost, there is still a long way to go before thermoelectric regrigeration can compete with the vapor compression system though for specialty devices, the thermoelectric system is unchallenged. It may also be noted that power supply constitutes an expensive item of expenditure in thermoelectric devices because it involves high currents at low voltages which is not as easy to arrange for.

Thermoelectric Materials

The figure of merit, Z, which involves the three thermoelectric parameters -- Seebeck coefficient, electrical resistivity and thermal conductivity -- is used for describing the merit of a thermoelectric material. Figure of merit is mathematically defined as $Z = \frac{S^2}{\rho K}$ where S = Seebeck coefficient, ρ = electric resistivity and K = thermal conductivity. It is evident that for a higher figure of merit, high Seebeck coefficient, high electrical conductivity and low thermal conductivity is required. In fact, all of these three parameters are functions of free electron concentration. It has been shown in Figure 3 that semiconductors have the highest figure of merit. In the past, only metals were used for thermoelectric applications, and since metals have a low figure of merit, the results were discouraging. The best thermocouple, chromel-constanton, such as used in temperature measurements has a Z value of about $0.1 \times 10^{-3} K^{-1}$ as given by Jaumont (12) and Eichhorn (13). In case of bismuth-antimony, couple Z may be about $0.23 \times 10^{-3} K^{-1}$.

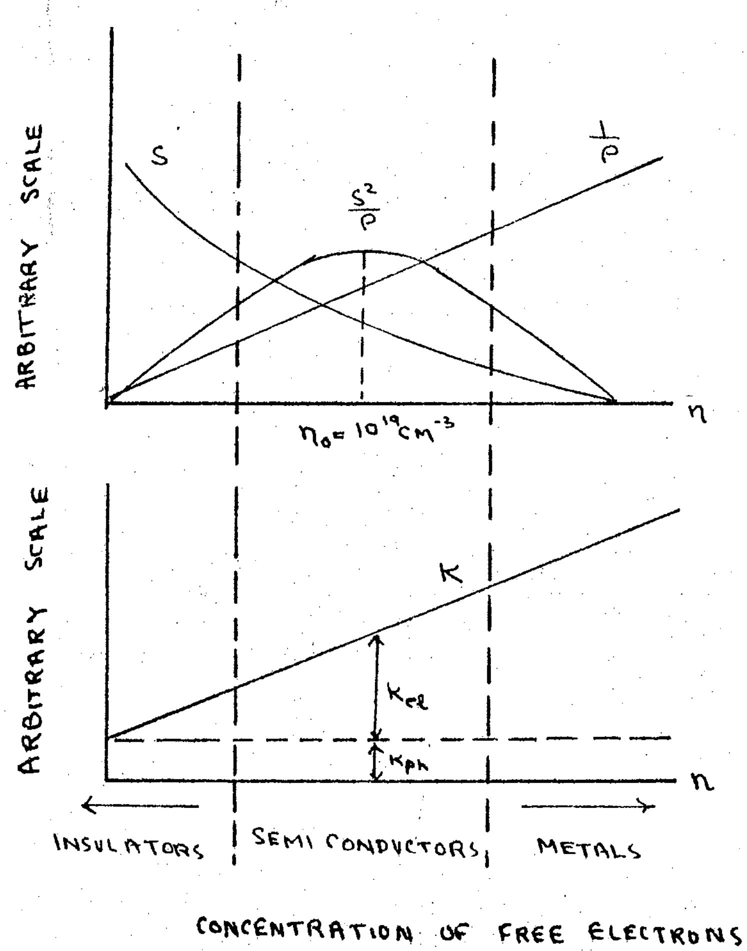


Figure 3. Effect of Free Electrons Concentration on Thermoelectric Parameters

Real progress in thermoelectric applications was achieved since semiconductors elements were tried as thermoelectric materials. The highest figures of merit have been obtained using either the compounds of lead with group VI elements or the V-VI compounds, bismuth telluride and lead telluride. Compounds of Sb, Se, S, may also prove good thermoelements.

Junctions of P-type Bi_2Te_3 and Bi have been prepared which give a maximum temperature difference of $40^{\circ}C$. Junctions of Bi_2Te_3 have frequently produced maximum temperature differences up to $60^{\circ}C$ whereas special junctions may give a 75-$80^{\circ}C$ difference as quoted by Kaye and Welsh (14). Russians have claimed that the elements produced as standard product give 55-$60^{\circ}C$ temperature difference, and special products give up to $80^{\circ}C$ difference.

Apart from the figure of merit, the thermoelectric materials are judged from the point of view of their auxiliary properties like melting point, vapor pressure, diffusion, oxidizability, coefficient of thermal expansion, compression and shear strength, etc.

Lead Telluride and its Alloys

Thermoelectric properties of lead telluride systems have been discussed in detail by Fritts and Richards (15) of Minnesota Mining and Manufacturing Company. The following text is extracted from the company's literature.

Lead telluride is a predominantly covalent intermetallic compound having a face centered cubic crystal structure. The pure compound has a melting point of $922^{\circ}C$ and contains 38.113 per cent by weight tellurium. PbTe occurs naturally as the mineral Altait, but PbTe of commercial significance is synthesized from its purified constituents.

PbTe is prepared by melting the constituents under hydrogen in a quartz container or by casting in carbon molds and rapidly cooling from the melt. Single crystals can also be grown easily. Stoichimetric excesses of Pb or Te in an otherwise pure crystal are soluble to the extent of only a few hundredths of one per cent. An excess of Pb solved into the crystal induces N-type electrical properties and an excess of Te induces P-type properties. The solubility of either component is somewhat temperature dependent. Physical properties of PbTe are listed on page 25.

Carrier concentrations of about 3×10^{17}/cc can be induced in PbTe by dissolving excess lead (N-type) or excess tellurium (P-type) into the crystal. An analysis of the figure of merit shows that the PbTe alloys of greatest interest for thermoelectric applications require both P-type and N-type carrier densities about an order of magnitude larger than those that can be obtained by solution of excess lead or tellurium alone. Such carrier densities can be attained by doping, that is by adding minute concentrations of certain foreign molecular species to the melt during preparation of the ingot. By means of doping P-type and N-type carrier densities can be increased up to 10^{19}/cc but beyond 10^{19}/cc any further increase in doping agent tends to decrease the electron and hole mobilities.

The thermoelectric properties -- Seebeck coefficient, electrical resistivity, and thermal conductivity -- of lead telluride systems are shown in Figures 4-8. These properties are essentially functions of temperature. The Seebeck coefficient of P-type and N-type lead telluride rise in magnitude with temperature to a maximum value beyond which further temperature rise causes intrinsic ionization to predominate and reduce this parameter. With increased doping, the extrinsic low temperature values of Seebeck coefficient are lowered, however, the temperature at which the Seebeck coefficient maximizes is shifted to higher values. Resistivity-temperature plots of P-type and N-type PbTe indicate a positive temperature coefficient at low and intermediate temperatures. At elevated temperatures the resistivity tends to decrease as intrinsic conduction becomes dominant. Increased doping reduces resistivity. Over the temperature range up to $600^{\circ}C$, the thermal conductivity can be described analytically as the sum of a lattice component, which decreases as with increasing temperature and a non degenerate hole conductivity.

Figure of merit, $Z = \frac{S^2}{K\rho}$, can be calculated from the three properties S, ρ, and K. At low temperatures, the highest Z values are provided by alloys containing lesser amounts of doping agents. At elevated temperatures, more heavily doped alloys provide the best Z values.

In view of their properties, PbTe alloy systems are by far the best thermoelements for generators. The successful operation of PbTe elements in thermoelectric generators at hot junction temperatures of $1100^{\circ}F$ has demonstrated the chemical stability of this component. These elements have delivered over-all efficiencies of 6% or slightly more.

Power Supply for Thermoelectric Devices

Thermoelectric devices are inherently high direct-current and very low voltage devices. A single stage cooling device may need as much as 100 amp d.c. at one tenth of a volt, depending on design parameters. The d.c. supply should be virtually free of ripples. Thus, one of the difficult questions posed by thermoelectric devices is that of power supply. Thermoelectric generators are ideally suited for supplying power to thermoelectric heat pumps because they would provide exactly the same type of supply as needed by the device. Transformers, rectifiers, and particularly filters are discouragingly bulky for such supply as mentioned by Vought (16).

When a.c. is used without perfect rectification, there is a loss in cooling capacity and coefficient of performance because the Joule heating will be determined by the rms value of current where Peltier cooling will be proportional to average d.c. value of current. Study of a refrigerator by Alfanso (17) indicates that ripple adversely affects the average temperature drop. Eichhorn (13) has estimated that with 10% ripple, loss in efficiency is about 4% which may be regarded as satisfactory.

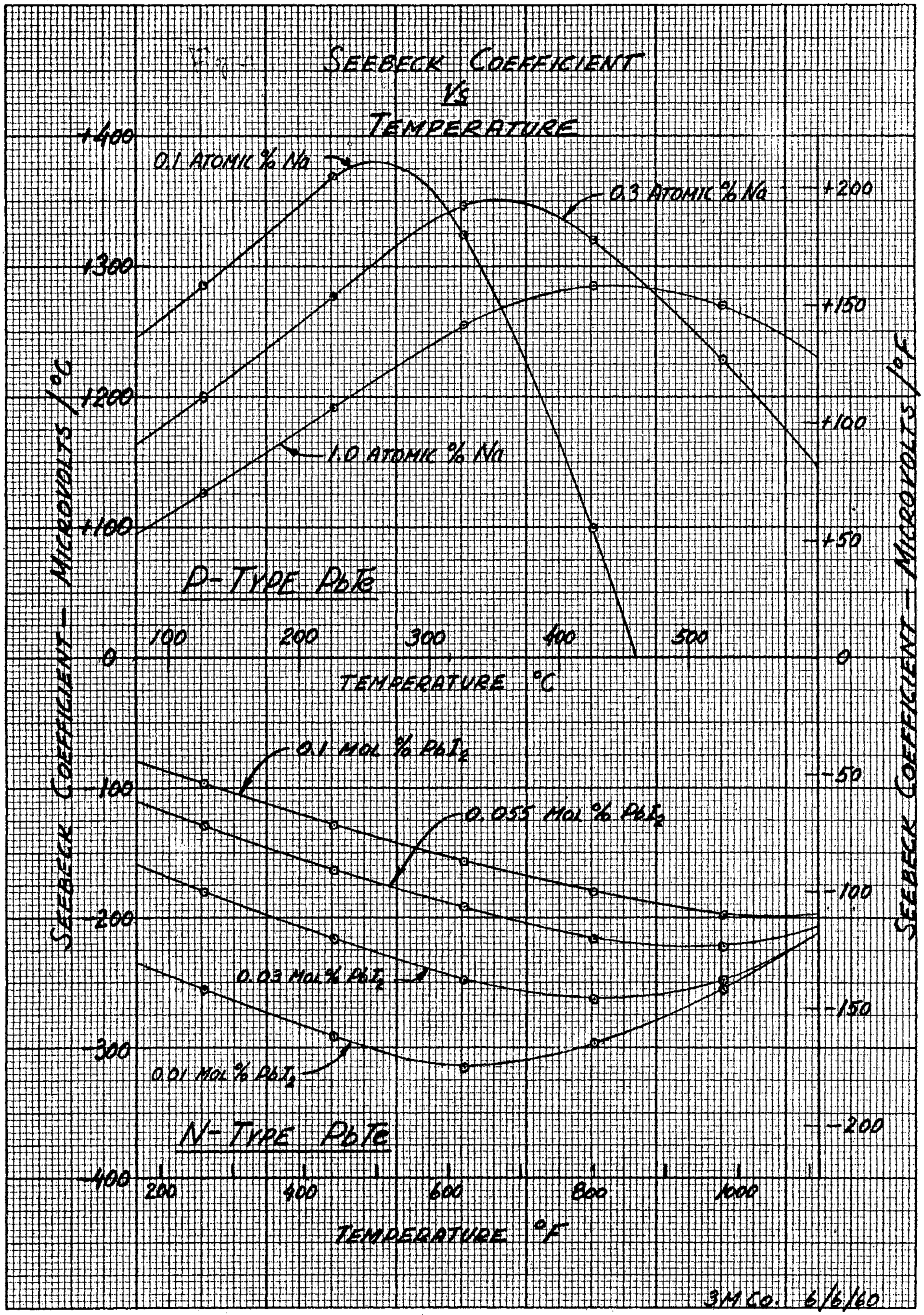


Figure 4. Seebeck Coefficient Versus Temperature Curve for P and N Type PbTe Alloys

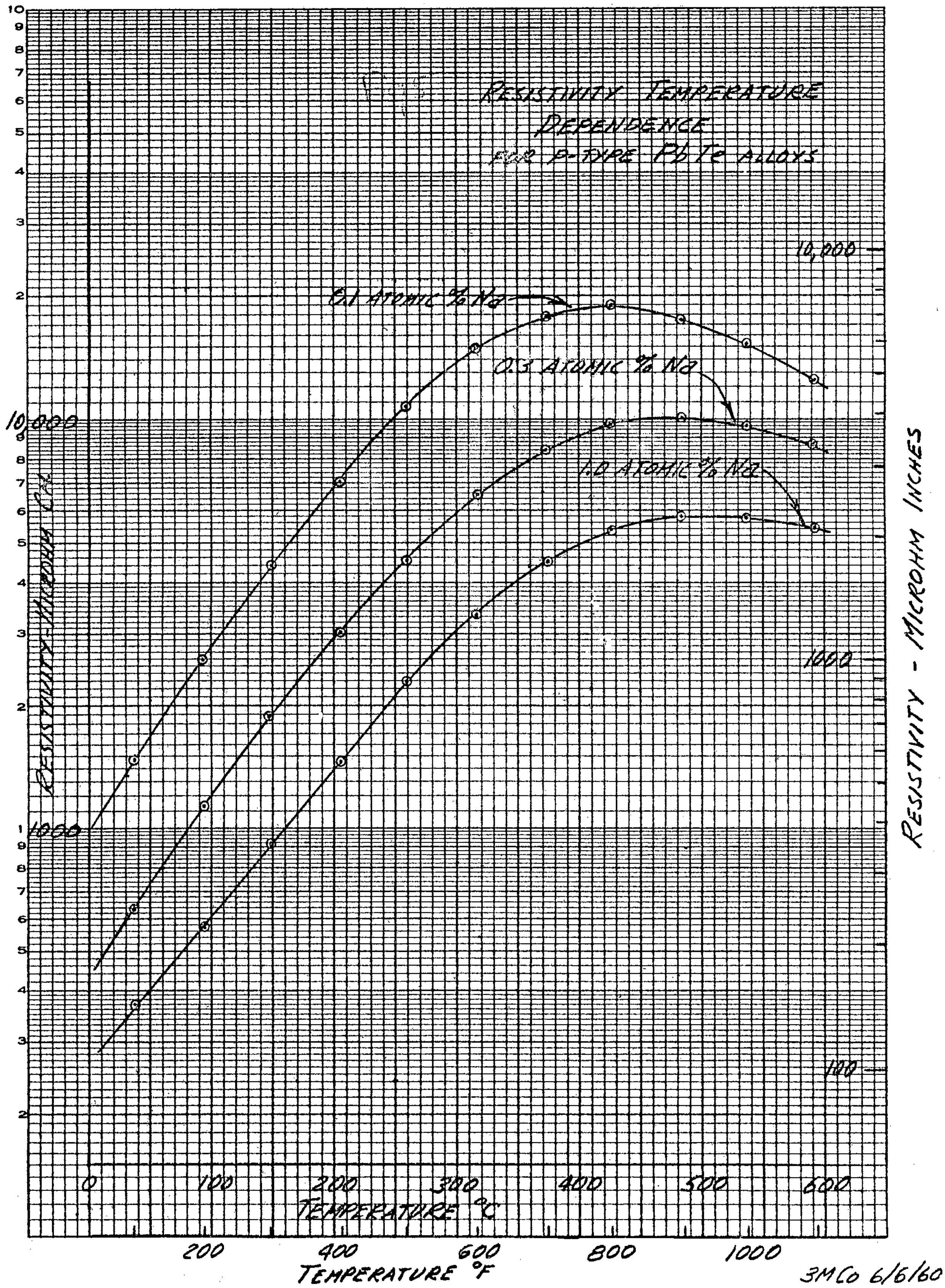


Figure 5. Resistivity Temperature Dependence for P-Type PbTe Alloys

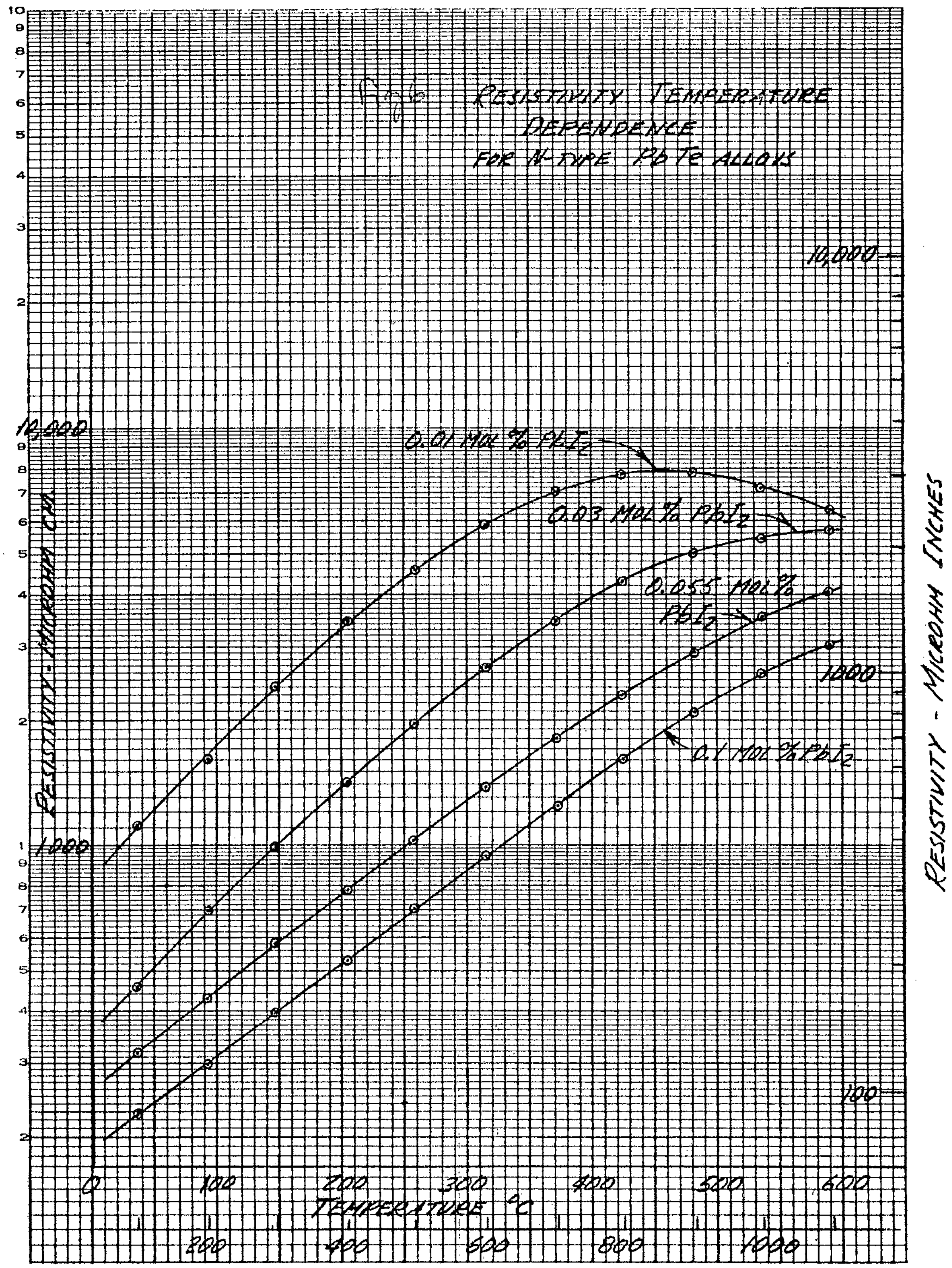


Figure 6. Resistivity Temperature Dependence for N-Type PbTe Alloys

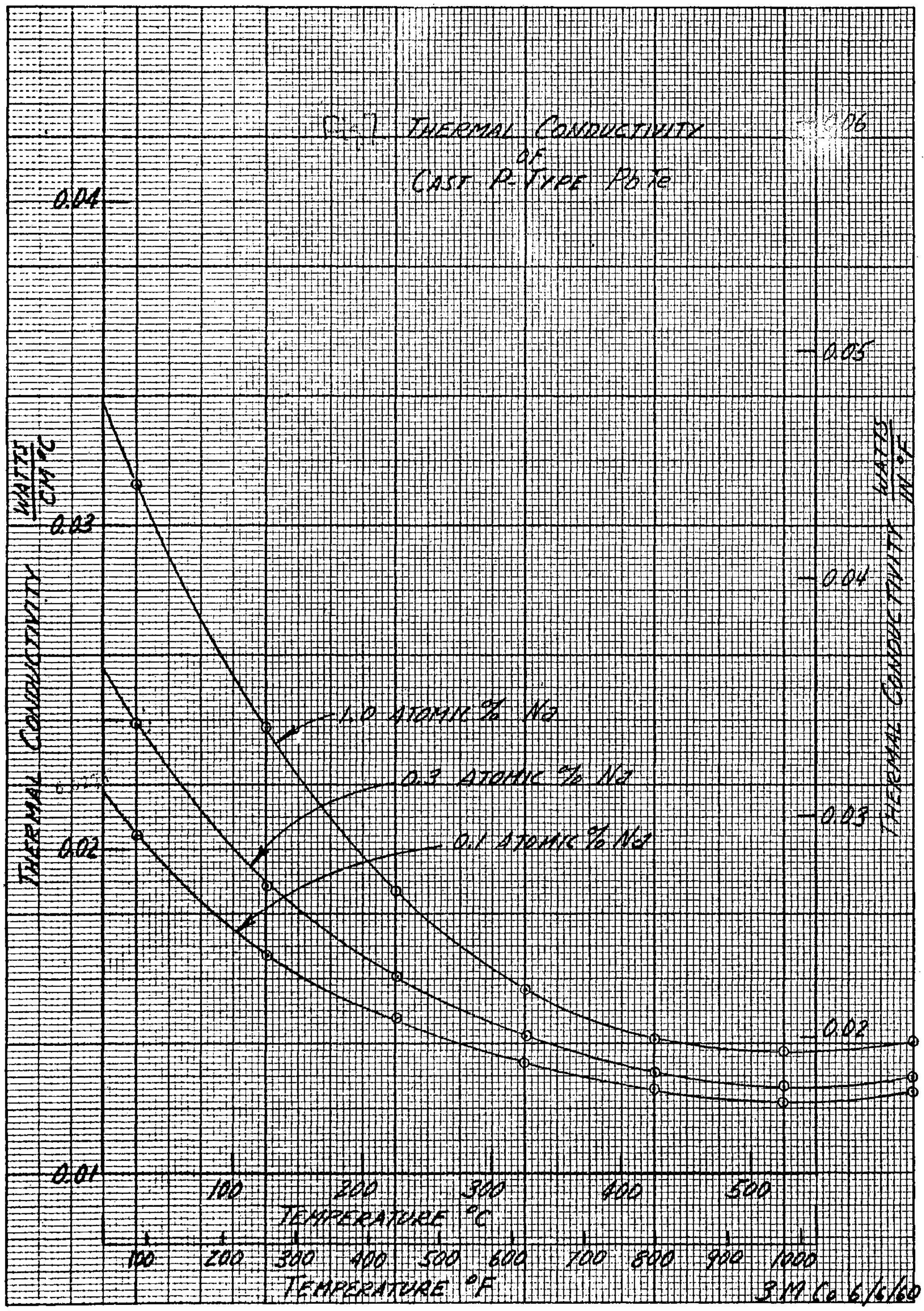


Figure 7. Thermal Conductivity-Temperature Curves for P-Type PbTe Alloys

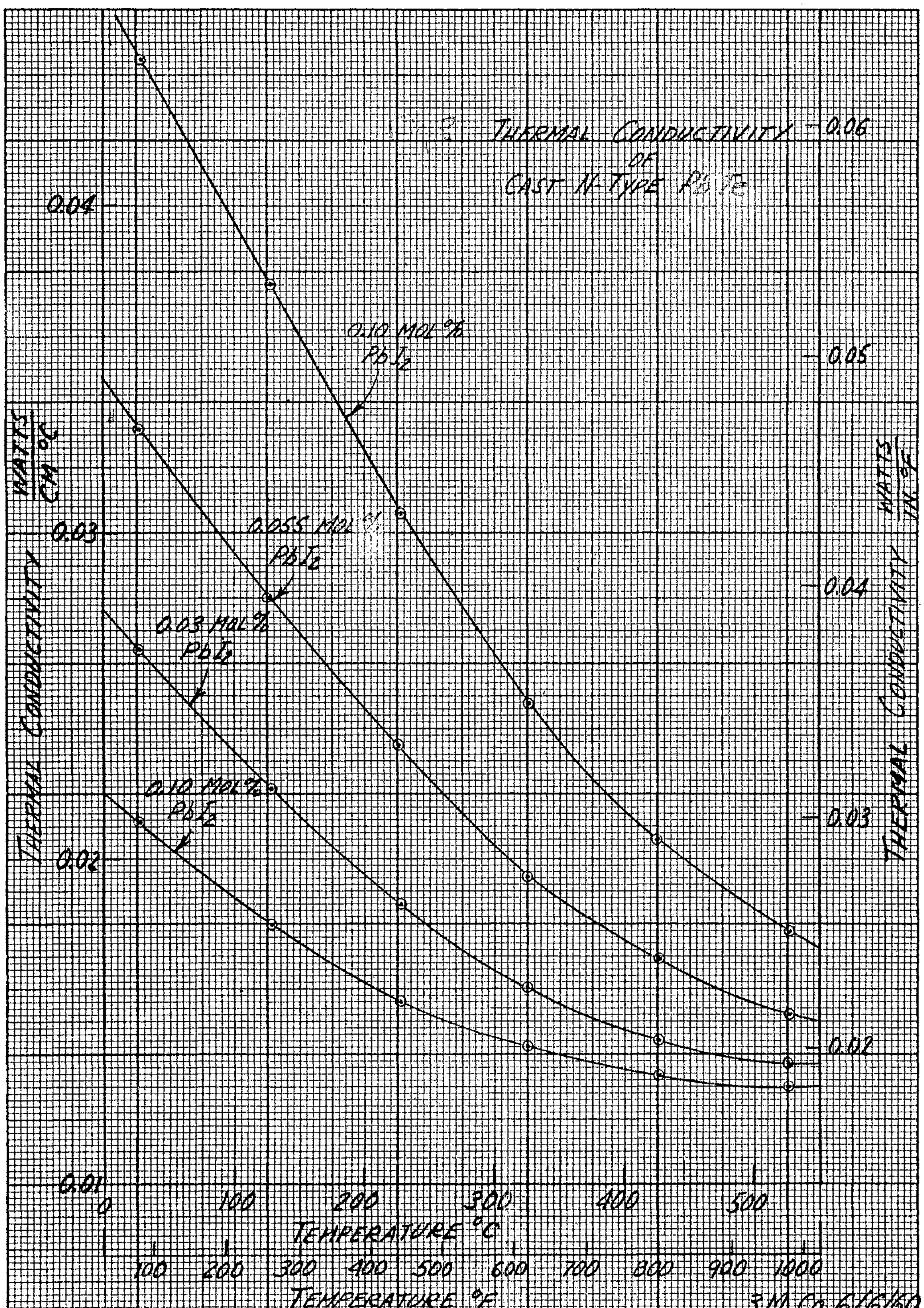


Figure 8. Thermal Conductivity-Temperature Curves for N-Type PbTe Alloys

CHAPTER II

MATHEMATICAL ANALYSIS OF DESIGN AND PERFORMANCE OF A THERMOELECTRIC COOLER

The following analysis of design was given by Ioffe (10) and has been followed in most of the textbooks. In this study, the symbols and sequence of analysis are those adopted by Cadoff (18).

The analysis is based on the following assumptions:

1. Over the range of temperature considered, the Seebeck coefficient S is independent of temperature.
2. The thermal conductivity and electrical conductivity are also independent of temperature.
3. The Thomson heat transfer rates are negligible with respect to the Peltier and other rates.
4. No heat is lost or gained through the walls and sides of the thermoelectric arms.

For the present, it is also assumed that:

5. Conductors and junctions are such as to have $S = 0$, $\rho = 0$, and $K = \infty$.
6. The cross sections and lengths of N and P type materials are equal.

Symbols

S = Seebeck coefficient	volts/deg
ρ = Electrical resistivity	ohm - cm

σ	= Electrical conductivity	$ohm^{-1} - cm^{-1}$
K_t	= Thermal conductivity	watts/cm-deg
Z	= Figure of merit $\frac{S^2}{\rho K_t}$	deg^{-1}
T	= Absolute temp	degrees Kelvin
π	= Peltier coefficient	volts
$\mathring{Q}$	= Rate of heat transfer	watts
R_i	= Total electrical resistance of two arms (N and P arms in series)	ohms
R_c	= Contact resistivity of cold junction	$ohm - cm^2$
K	= Total thermal conductance of two arms in parallel	watts/deg
I	= Current	amps
ΔT	= $T_h - T_c$ = Temperature difference across couple	deg
φ	= $\frac{\mathring{Q}}{P}$ Coefficient of performance	numerical value
P	= IV Power input	watts
l	= Length of arm	cm
a	= Cross section area of arm	cm^2
y	= $\frac{\text{area}}{\text{length}}$ factor	cm

The rate of heat transfer from cold to hot junction by the Peltier effect is:

$$\mathring{Q}_{\pi} = \pi I = ST_c I \text{ where } S = /S_n/ + /S_p/ .$$

As R and K are independent of temperature, the Joule heat is assumed to be equally distributed at each junction; also there is some heat lost in conduction from the hot junction along the legs to the cold junction. Hence, the net rate of heat removal, i.e., the heat pumping

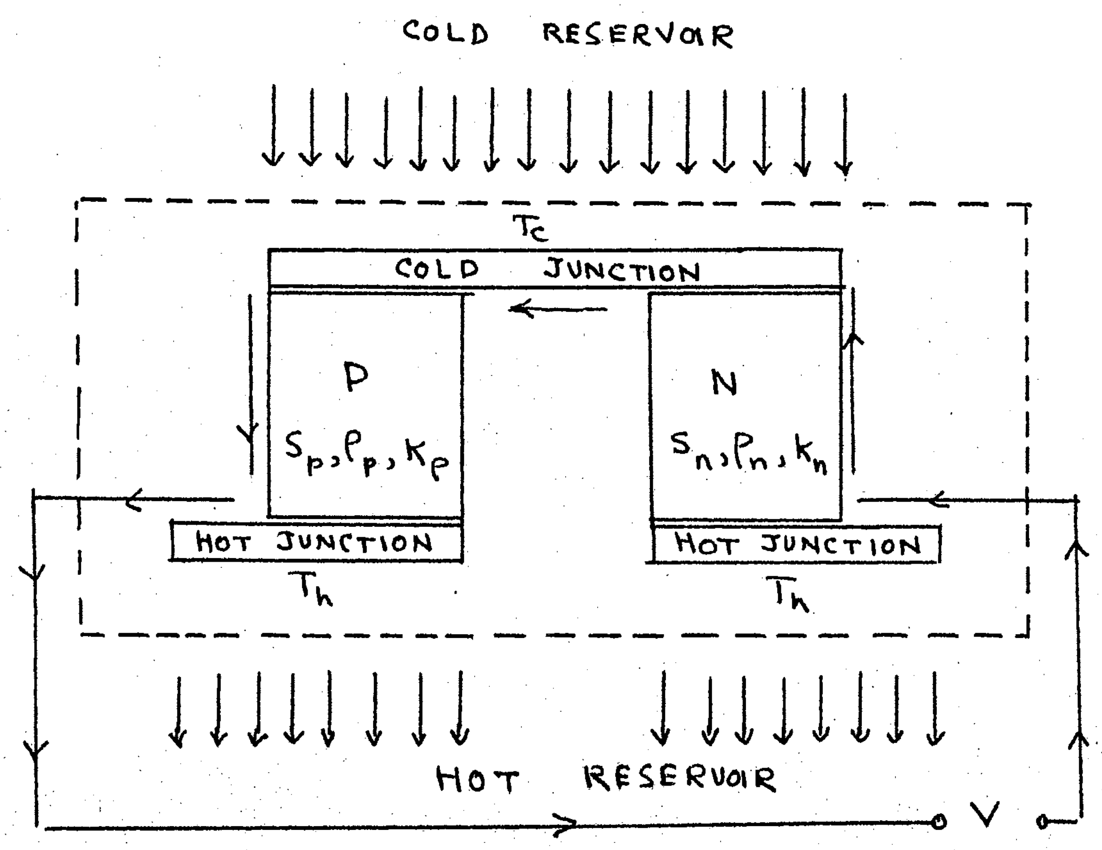


Figure 9. Diagramatic Representation of a Single Stage Thermoelectric Cooler

capacity is:

$$\dot{Q} = \dot{Q}_{\pi} - \tfrac{1}{2}Q_{j} - Q \text{ cond}$$

$$= ST_{c}I - \tfrac{1}{2}I^{2}R_{i} - K \Delta T . \quad (1)$$

In order to find out the current required for maximum cooling, one may differentiate $\dot{Q}$ with respect to I and equate it to zero.

$$\frac{d\dot{Q}}{dI} = ST_{c} - \tfrac{1}{2}x2I\ R_{i} - 0 = 0$$

$$\therefore I_{\dot{Q}} = \frac{ST_{c}}{R_{i}} \quad (2)$$

where $I_{\dot{Q}}$ is the current giving maximum cooling.

If this current is used with the cold junction thermally insulated ($\dot{Q} = 0$), one gets the maximum temperature difference.

$$0 = ST_{c} \cdot \frac{ST_{c}}{R_{i}} - \tfrac{1}{2}\left(\frac{ST_{c}}{R_{i}}\right)^{2} \cdot R_{i} - K\Delta T_{m}$$

$$\therefore \Delta T_{m} = \tfrac{1}{2}\frac{S^{2}}{R_{i}} \cdot T_{c}^{2} \cdot \frac{1}{K}$$

$$\Delta T_{m} = \tfrac{1}{2} Z_{c}\ T_{c}^{2} \quad (3)$$

where Z_{c} = figure of merit of the couple (not material).

Substituting the value of optimum current from Equation (2) in Equation (1),

$$\dot{Q} \max = ST_{c} \times \frac{ST_{c}}{R_{i}} - \tfrac{1}{2}\left(\frac{ST_{c}}{R_{i}}\right)^{2} \times R_{i} - K\,\Delta T$$

$$= \tfrac{1}{2}\frac{S^{2}T_{c}^{2}}{R_{i}} - K\,\Delta T \quad (4)$$

$$= \tfrac{1}{2}\,Z_{c}\ T_{c}^{2} \cdot K - K\,\Delta T .$$

But from Equation (3), it is known that $\Delta T_m = \frac{1}{2} Z_c^{\,2} T_c^{\,2}$, so

$$\dot{Q}\ max = K\Delta T_m - K\Delta T$$

$$= K(\Delta T_m - \Delta T)$$

$$\dot{Q}\ max = K\Delta T_m \left(1 - \frac{\Delta T}{\Delta T_m}\right) . \tag{5}$$

The power required to pump heat at the rate $\dot{Q}$ is

$$P = IS\Delta T + I^2 R_i \tag{6}$$

$$= \frac{ST_c}{R_i} \cdot S \cdot \Delta T + \left(\frac{ST_c}{R_i}\right)^2 R_i$$

$$= \frac{S^2 T_c}{R_i} \cdot \Delta T + \frac{S^2 T_c^{\,2}}{R_i} .$$

But $\frac{S^2 T_c^{\,2}}{R_i} = 2K\Delta T_m$.

$$\therefore P = \frac{2K\Delta T_m}{T_c} \Delta T + 2K\Delta T_m$$

$$P = 2K\Delta T_m \left(1 + \frac{\Delta T}{T_c}\right) . \tag{7}$$

Using this value of P with $\dot{Q}$ from Equation (5), the coefficient of performance when the current is adjusted for maximum heat pumping is

$$\varphi_{\dot{Q}} = \frac{\dot{Q}_m}{P}$$

$$= \frac{K\Delta T_m \left(1 - \frac{\Delta T}{\Delta T_m}\right)}{2K\Delta T_m \left(1 + \frac{\Delta T}{T_c}\right)}$$

$$= \frac{1 - \frac{\Delta T}{\Delta T_m}}{2\left(1 + \frac{\Delta T}{T_c}\right)} \simeq \frac{1}{2} \left(1 - \frac{\Delta T}{\Delta T_m}\right)\left(1 - \frac{\Delta T}{T_h}\right) . \tag{8}$$

The analysis just stated was for a thermoelectric couple operated at maximum heat pumping capacity. If the couple is desired to be operated at maximum coefficient of performance, the following mathematical treatment will hold.

$$\varphi \text{ (coefficient of performance)} = \frac{\dot{Q}}{P} \; .$$

Substituting the values of $\dot{Q}$ and P from Equations (1) and (6),

$$\varphi = \frac{ST_c I - \frac{1}{2} I^2 R_i - K\Delta T}{IS\Delta T + I^2 R_i} \; .$$

For maximum coefficient of performance, this equation is differentiated with respect to I and equated to zero,

$$\frac{d\varphi}{dI} = \frac{d}{dI}\left(\frac{ST_c I - \frac{1}{2} I^2 R_i - K\Delta T}{IS\Delta T + I^2 R_i}\right) = 0.$$

After manipulations, the result is:

$$I_\varphi \text{ (current for max. COP)} = \frac{ST_c}{R_i}\,\frac{\Delta T}{\Delta T_m} \cdot A \qquad (9)$$

$$\text{or } I_\varphi = I_{\dot{Q}}\,\frac{\Delta T}{\Delta T_m} \cdot A \qquad (9a)$$

where A is a factor close to unity, given by

$$A = \frac{1 + \left(1 + 2\,\frac{\Delta T_m}{T_c} + \frac{\Delta T \Delta T_m}{T_c^{\,2}}\right)^{1/2}}{2 + \frac{\Delta T}{T_c}} \qquad (10)$$

Assuming A equal to unity, one gets

$$I_\varphi = I_{\dot{Q}} \frac{\Delta T}{\Delta T_m} . \tag{9b}$$

With this current, the cooling capacity is, using Equation (9a) in (1),

$$\dot{Q}_\varphi = K\Delta T \left(2A - \frac{\Delta T}{\Delta T_m} A^2 - 1\right) . \tag{11}$$

If A is regarded as unity,

$$\dot{Q}_\varphi = K\Delta T \left(1 - \frac{\Delta T}{\Delta T_m}\right) \tag{11a}$$

which can be written in terms of maximum cooling capacity

$$\dot{Q}_\varphi = \frac{\Delta T}{\Delta T_m} \dot{Q}_m . \tag{11b}$$

The coefficient of performance when using this current expressed just previous becomes

$$\varphi_m = \frac{2 - \frac{1}{A} - \frac{\Delta T}{\Delta T_m} A}{2\left(\frac{\Delta T}{T_c} + \frac{\Delta T}{\Delta T_m} A\right)} . \tag{12}$$

If A is assumed to be unity,

$$\varphi_m = \frac{1 - \frac{\Delta T}{\Delta T_m}}{2\left(\frac{\Delta T}{\Delta T_m} + \frac{\Delta T}{T_c}\right)} \tag{12a}$$

which may be written

$$\varphi_m = \frac{\Delta T_m}{\Delta T} \cdot ½ \left(1 - \frac{\Delta T}{\Delta T_m}\right)\left(1 - \frac{\Delta T}{T_h}\right) \frac{1}{1 + \frac{\Delta T_{m} - \Delta T}{T_h}} \tag{12b}$$

This, comparing with Equation (8) is very nearly

$$\varphi_m = \frac{\Delta T_m}{\Delta T} \cdot \varphi_{\dot{Q}} \quad . \tag{12c}$$

This ratio $\frac{\Delta T}{\Delta T_m}$ is seen to be very nearly the ratio of corresponding quantities for the two types of operation - maximum cooling and maximum coefficient of performance.

When the values of resistivity (ρ) and thermal conductivity (K) for the P and N legs are not the same,

$$Z = \left\{\frac{/S_p/ + /S_n/}{\sqrt{\frac{K_n}{\sigma_p}} + \sqrt{\frac{K_n}{\sigma_p}}}\right\}^2 \quad . \tag{13}$$

The maximum coefficient of performance stated in Equation (12) can also be expressed by the following expression:

$$\varphi_m = \frac{T_c}{T_h - T_c} \cdot \frac{\sqrt{1 + Z\frac{T_h + T_c}{2}} - \frac{T_h}{T_c}}{\sqrt{1 + Z\frac{T_h + T_c}{2}} + 1} \quad . \tag{12d}$$

CHAPTER III

DESIGN OF A COOLER, USING THE THERMOELECTRIC ELEMENTS TYPE TEG MANUFACTURED BY 3M COMPANY

Design Conditions

- Cooler to remove 5 watts of heat (17 BTU/hr)
- Temperature at which cold chamber is to be held −5°C (268°K)
- Temperature of heat sink available 25°C (298°K)

Thus

$$\dot{Q} = 5 \text{ watts}$$

$$T_c = 268°K$$

$$T_h = 298°K$$

$$\Delta T = 30°K.$$

Material Properties

Lead Telluride thermoelements type TEG, manufactured by Minnesota Mining and Manufacturing Company, have the following properties:

Seebeck coefficient:

$S = /S_p/ + /S_n/ = 12$ milli volts for a temperature difference of 30°C, or

$$S = \frac{12 \times 10^{-3}}{30} = 400 \text{ micro volts per °C.}$$

The value of S was found from the graph applied by the manufacturer which is reproduced on page (26) of this report.

Electrical Resistivity

TEG #2P Element:

$$\rho_p = 150 \text{ micro ohm inch}$$

$$= 150 \times 2.54 = 382 \times 10^{-6} \text{ ohm cm}$$

TEG #2N Element:

$$\rho_n = 200 \text{ micro ohm inch}$$

$$= 200 \times 2.54 = 508 \times 10^{-6} \text{ ohm cm.}$$

The values of ρ_p and ρ_n are taken from the graph given by the manufacturer and shown on page (26) of this report.

Since the P and N elements are in series,

$$\text{Resistivity of the elements} = (382 + 508)\ 10^{-6}$$

$$= 0.89 \times 10^{-3} \text{ ohm cm.}$$

Thermal Conductivity

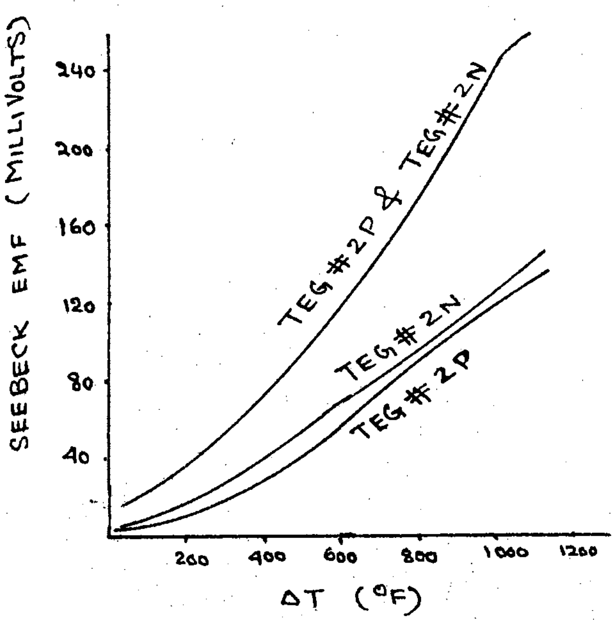
The thermal conductivity is given in manufacturer's literature as 0.02 watts/cm/°C for both TEG #2P and TEG #2N elements.

$$K_t = 2 \cdot 10^{-2} \text{ watts/cm/°C.}$$

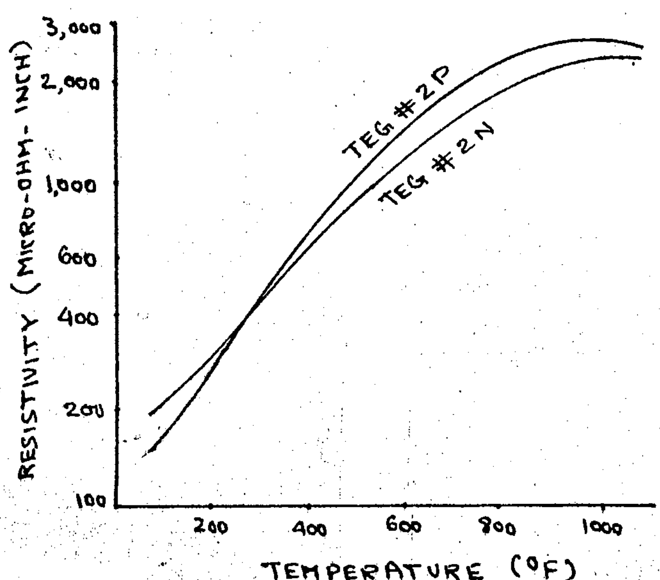
Physical Properties

Manufacturers have given the following physical properties for the elements:

	TEG #2P	TEG #2N
Tensile strength	$>$ 1000 Psi	$>$ 1000 Psi
Compression strength	$>$ 10,000 Psi	$>$ 10,000 Psi
Young's Modulus	2×10^6 Psi	2×10^6 Psi



(a) Seebeck Voltage Versus Temperature Difference



(b) Resistivity Versus Temperature Curves

Figure 10. Thermoelectric Properties of Elements Type TEG #2 of 3M Company

Density	8 · 15 g/cc	8 · 15 g/cc
Thermal expansion coefficient	$18 \times 10^{-6}/°C$	$18 \times 10^{-6}/°C$
Standard dimensional tolerance	$\pm$ 0.005 in	$\pm$ 0.005 in

Design Calculations for a Cooler Having

Maximum Cooling Capacity

(1) With the known values of S_p, S_n, ρ_p, ρ_n, and K, figure of merit Z is calculated:

$$Z = \left[\frac{/S_p/ + /S_n/}{\sqrt{K_p \rho_p} + \sqrt{K_n \rho_n}}\right]^2$$

$$= \left[\frac{400 \times 10^{-6}}{\sqrt{2 \times 10^{-2} \times 382 \times 10^{-6}} + \sqrt{2 \times 10^{-2} \times 508 \times 10^{-6}}}\right]^2$$

$$= \left[\frac{400 \times 10^{-6}}{\sqrt{2 \times 10^{-2} \times 10^{-6}}\,(\sqrt{382} + \sqrt{508})}\right]^2$$

$$= \frac{16 \times 10^{-8}}{2 \times 10^{-8}(19.5 + 22.5)^2}$$

$$= \frac{8}{(42)^2} \qquad = 4.54 \times 10^{-3} .$$

This is the figure of merit when the junction and lead resistivity are neglected. It is assumed that figure of merit is reduced by 10 per cent due mainly to the junction resistance. Then,

Z_c (figure of merit of the couple)

$$= 4.54 \times 10^{-3} \times 0.9 = 4.1 \times 10^{-3} \text{ deg}^{-1}$$

(2) With the known value of Z_c and T_c and using Equation (3), one may calculate the maximum temperature difference that can be obtained theoretically from this couple.

$$\Delta T_m = \tfrac{1}{2} Z_c (T_c)^2$$

$$= \tfrac{1}{2} \times 4.1 \times 10^{-3} \times (268)^2$$

$$= 144°C \ .$$

(3) Having known the values of ΔT_m and ΔT, coefficient of performance for this cooler with maximum cooling capacity can be found using Equation (8).

$$\varphi_{\dot{Q}} = \tfrac{1}{2}(1 - \frac{\Delta T}{\Delta T_m})(1 - \frac{\Delta T}{T_h})$$

$$= \tfrac{1}{2}(1 - \frac{30}{144})(1 - \frac{30}{298})$$

$$= \tfrac{1}{2}(1 - 0.21)(1 - 0.101)$$

$$= \tfrac{1}{2} \times 0.79 \times 0.899$$

$$= 0.355.$$

(4). The rate of heat transfer is assumed to be 5W as per these design conditions; now in Equation (5) all are known except K, which is evaluated:

$$\dot{Q}_m = K \Delta T_m (1 - \frac{\Delta T}{\Delta T_m})$$

$$5 = K \cdot 144 (1 - \frac{30}{144})$$

$$= K \cdot 144 \cdot 0.79 \ .$$

$$\therefore K = \frac{5}{144 \times 0.79} = 0.044 \text{ watts/deg.}$$

This is the total thermal conductance through both arms.

(5) The values of K and K_t (assumed to be given as 2×10^{-2} watts/cm deg) now fix the ratio $\frac{\text{area}}{\text{length}}$ which is denoted as Y.

$$Y = \frac{\text{area}}{\text{length}} = \frac{K}{2K_t}$$

$$= \frac{0.044}{2 \times 2 \times 10^{-2}} = 1.1 \text{ cm.}$$

(6) This value of Y and assumed value for total resistivity $\rho = 0.89 \times 10^{-3}$ ohm cm determine the total series resistance of the arms:

$$R_i = \frac{\rho_1}{a} = \frac{\rho}{y} = \frac{0.89 \times 10^{-3}}{1.1} = 0.808 \times 10^{-3} \text{ ohm.}$$

(7) Now in Equation (2), S, T_c and R_i are known and their values are substituted to find $I_{\dot{Q}}$:

$$I_{\dot{Q}} = \frac{ST_c}{R_i} = \frac{400 \times 10^{-6} \times 268}{0.808 \times 10^{-3}}$$

$$= 133 \text{ amps.}$$

(8) Voltage of the supply can be found, knowing the current and resistance of the arms:

$$V = IR$$

$$= 133 \times 0.808 \times 10^{-3}$$

$$= 0.107 \text{ volts.}$$

Junction Resistance

In Chapter II, while discussing the mathematical analysis of thermoelectric cooling, junction and copper connector resistances were assumed to be negligible. In practice, junction resistance is not only accountable, but it is an important criterion in designing the dimensions of the device. As shown in the previous section (Step 5), the design parameters determine only the factor Y (ratio of area to length) of the arms. Theoretically, a small couple will satisfy the design conditions as well as a large one as long as the value of 'Y' does not change. Thus, it is possible to reduce both length and cross sectional area of arms at the same time, keeping their ratio constant. Practically, it is not possible. The limit is set by contact resistance and fabrication techniques.

In this section, it is shown how the junction resistance sets the limitations on the dimension of the device and determines the minimum length of the arms. For this analysis, the procedure adopted by Cadoff (18) has been followed.

The resistance of the connectors which may be of copper is many orders of magnitude lower than that of thermoelectric materials; thus, its effects can be kept very low, say below one per cent. The effect of junction resistances, especially that of cold junction, is quite significant. The heat generated at cold junction effectively adds to the heat load, whereas heat at hot junction is quite close to the heat rejecting surface and may be negligible.

Let Rj = resistance of one cold junction.

$\therefore$ Heat loss in two junctions = $2\ I^2\ Rj$.

Let R_i = total resistance of thermoelements.

Assuming that half of the Joule heat is to be removed from cold junction, the total heat from cold junction

$$= \frac{1}{2} I^2 R_i + 2 I^2 Rj$$

$$= \frac{1}{2} I^2 (R_i + 4 Rj).$$

Effective resistance of the couple for cooling purposes will be R_i + 4Rj and the effective figure of merit would be:

$$Z'c = \frac{S^2}{(R_i + 4Rj)K} = \frac{S^2}{R_i K} \times \frac{1}{1 + \frac{4R_j}{R_i}}$$

$$= Zc \times \frac{1}{1 + \frac{4R_j}{R_i}} .$$

In the previous calculations on page 27, it was assumed that Z_c was 0.9 times the figure of merit of the material. In other words, a provision of 10 per cent decrease in figure of merit was made which allowed for junction resistance, copper connections, etc. When considering only the cold junction resistance, it can be assumed that a decrease of 8 per cent in the figure of merit is caused due to cold junction resistance. Then

$$\frac{Z'_c}{Z_c} = \frac{1}{1 + \frac{4R_j}{R_i}}$$

$$\frac{92}{100} = \frac{1}{1 + \frac{4R_j}{R_i}}$$

$$\therefore \frac{R_j}{R_i} = \tfrac{1}{4}\left(\frac{100}{92} - 1\right)$$

$$= \tfrac{1}{4}\,(1.087-1) = 0.0218.$$

Let R_c = contact resistivity of the junction

$$\therefore R_j = \frac{R_c}{a} \quad \text{where } a = \text{cross section area of arm.}$$

Again $R_l = \rho\frac{l}{a}$ where ρ = resistivity of thermoelements.

Substituting the values of R_j and R_i, gives

$$\frac{\frac{R_c}{a}}{\rho\,\frac{l}{a}} = 0.0218$$

$$\therefore l = \frac{R_c}{\rho} \times \frac{1}{0.0218}.$$

The material used here has:

$\rho = 0.89 \times 10^{-3}$ as given on page (25).

In practice contact resistivity of 10^{-5} ohm - cm^2 is generally obtainable with the special techniques and methods of fabricating junction of thermoelectric devices. (18). Assuming $R_c = 10^{-5}$ ohm - cm^2 gives

$$l = \frac{10^{-5}}{0.89 \times 10^{-3}} \times \frac{1}{0.0218}$$

$$= 0.516 \text{ cm.}$$

This is the optimum length of the arms of the cooler under the assumptions made.

Dimensions of the cooler:

The value of 'Y' $\left(\frac{\text{area}}{\text{length}}\right.$ factor) was found on page 29 to be 1.1 cm.

Now adopting the length of 0.516 for the cooler arms,

A (area of cross section) = 0.516 x 1.1

= 0.5676 cm.

Total volume of thermoelectric material

$= 2\ a\ l$

$= 2 \times 0.5676 \times 0.516$

$= 0.585\ cm^3.$

Design Calculations for a Cooler Having Maximum Coefficient of Performance

(1) Figure of merit 'Z' will be the same as calculated for the cooler of maximum cooling capacity.

$$Z = 4.54 \times 10^{-3}\ deg^{-1}.$$

Again, assuming a 10 per cent decrease due to junction resistance and copper connector,

$$Z_c = 4.54 \times 10^{-3} \times 0.9$$

$$= 4.1 \times 10^{-3}\ deg^{-1}.$$

(2) The theoretical maximum temperature difference ΔT_m will be the same as calculated for the cooler of maximum cooling capacity,

$$\Delta T_m = \tfrac{1}{2}\ Z_c\ (T_c)^2$$

$$= \tfrac{1}{2} \times 4.1 \times 10^{-3} \times (268)^2 = 144°C.$$

(3) For calculating the coefficient of performance, Equation (12) is used:

$$\varphi_m = \frac{2 - \frac{1}{A} - \frac{\Delta T}{\Delta T_m} \cdot A}{2 \; \frac{\Delta T}{T_c} + \frac{\Delta T}{\Delta T_m} \; A)}$$

where

$$A = \frac{1 + (1 + \frac{2\Delta T_m}{T_c} + \frac{\Delta T \Delta T_m}{T_c^2})^{1/2}}{2 + \frac{\Delta T}{T_c}} \; .$$

Putting in the known values gives

$$A = \frac{1 + (1 + 2\,\frac{144}{268} + \frac{30 \times 144}{(268)^2})^{1/2}}{2 + \frac{30}{268}}$$

$$= \frac{1 + (1 + 1.072 + 0.0605)^{1/2}}{2 + 0.112}$$

$$= \frac{1 + \sqrt{2.132}}{2.112} = \frac{1 + 1.46}{2.112} = 1.17.$$

$$\varphi_m = \frac{2 - \frac{1}{1.17} - \frac{30}{144} \times 1.17}{2\left(\frac{30}{268} + \frac{30}{144} \times 1.17\right)}$$

$$= \frac{2 - 0.855 - 0.244}{2\;(0.111 + 0.244)}$$

$$= \frac{0.911}{2 \times 0.355} = 1.29.$$

In case Equation (12b) is adopted, which assumes $A = 1$, the following results:

$$\varphi_m = \frac{\Delta T_m}{\Delta T} \cdot \; \tfrac{1}{2}(1 - \frac{\Delta T}{\Delta T_m})(1 - \frac{\Delta T}{T_h}) \; \frac{1}{1 + \frac{\Delta T_m - \Delta T}{T_h}}$$

$$= \frac{144}{30} \cdot \tfrac{1}{2}\left(1 - \frac{30}{144}\right)\left(1 - \frac{30}{298}\right) \frac{1}{1 + \frac{144 - 30}{298}}$$

$$= \frac{144}{60} \cdot \frac{114}{144} \cdot \frac{268}{298} \cdot \frac{298}{298 + 116}$$

$$= 1.23.$$

If, instead of applying the exact formulae, the simplified Equation (12c) had been adopted, assuming A to be unity and making other approximations, the result would have been:

$$\varphi_m = \frac{\Delta T_m}{\Delta T} \varphi_{\dot{Q}}$$

$$= \frac{144}{30} \times 0.355$$

$$= 1.7.$$

If Equation (12d) is applied, which is yet another exact form of expression for φ_m, the result is:

$$\varphi_m = \frac{T_c}{T_h - T_c} \cdot \frac{\sqrt{1 + Z\frac{(T_h + T_c)}{2}} - \frac{T_h}{T_c}}{\sqrt{1 + Z\frac{(T_h + T_c)}{2}} + 1}$$

$$= \frac{268}{298 - 268} \cdot \frac{\sqrt{1 + 4.1 \times 10^{-3}\left(\frac{298 + 268}{2}\right)} - \frac{298}{268}}{\sqrt{1 + 4.1 \times 10^{-3}\left(\frac{298 + 268}{2}\right)} + 1}$$

$$= \frac{268}{30} \cdot \frac{\sqrt{1 + 4.1 \times 10^{-3} \times 283} - 1.11}{\sqrt{1 + 4.1 \times 10^{-3} \times 283} + 1}$$

$$= 8.933 \cdot \frac{\sqrt{1 + 1.16} - 1.11}{\sqrt{1 + 1.16} + 1}$$

$$= 8.933 \cdot \frac{1.465 - 1.11}{1.465 + 1}$$

$$= 8.933 \cdot \frac{0.355}{2.465} = 1.29.$$

Note: The coefficient of performance was calculated adopting different mathematical formulae in order to compare the results and judge their accuracies. The expression (12) and (12d) are the same equations, but given in terms of different parameters. Thus, the results obtained through these equations are the same. Equation (12b) where 'A' was assumed to be unity is a good approximation which gave a not too different result, whereas equation (12c) may be regarded as a very rough approximation.

The maximum theoretical coefficient of performance that can ever be achieved for a cooler operating between the assumed range of temperature difference is given by the COP of Carnot engine which is $\frac{Tc}{Th - Tc}$. Its value was found in the proceeding calculations to be 8.933.

(4) In order to determine thermal conductance, expression (11) is used in which all the values are known except K.

$$Q_{\varphi} = K\Delta T\,(2A - \frac{\Delta T}{\Delta T_m} A^2 - 1)$$

$$5 = K \cdot 30\ (2 \times 1.17 - \frac{30}{144} (1.17)^2 - 1)$$

$$5 = K \cdot 30\,(2.34 - 0.285 - 1)$$

$$\therefore K = \frac{5}{30 \times 1.055} = 0.158 \text{ watt/deg.}$$

(5) The value of K and the known value of K_t are used to determine 'Y' as was done in the previous design.

$$Y = \frac{K}{2K_t} = \frac{0.158}{2 \times 2.10^{-2}} = 3.95 \text{ cm.}$$

(6) The known value Y and P specify the total resistance of the couple R_i.

$$R_i = \frac{\rho}{Y} = \frac{0.89 \times 10^{-3}}{3.95} = 0.225 \times 10^{-3} \text{ ohm.}$$

(7) Now, in Equation (9), the values of S, T_c, R_i, ΔT, ΔT_m, and A are all known. Hence, the value of current can be determined:

$$I_\varphi = \frac{St_c}{R_i} \cdot \frac{\Delta T}{\Delta T_m} \cdot A$$

$$= \frac{400 \times 10^{-6} \times 268}{0.225 \times 10^{-3}} \cdot \frac{30}{144} \cdot 1.17$$

$$= 116 \text{ amps.}$$

(8) Supply voltage can be found as current and resistance of the arms are now known.

$$V = IR$$

$$= 116 \times 0.225 \times 10^{-3}$$

$$= 0.0262 \text{ volts.}$$

Note: In the above calculations, exact equations are adopted for finding out the values of K, Y, R_i, and I without any approximation by assuming A = 1. If instead of the exact method, the approximate method had been adopted by assuming A = 1 and used in the simplified expressions, the result would be:

$$Q_{\varphi} = K\Delta T\,(1 - \frac{\Delta T}{\Delta T_m})$$

$$5 = K \cdot 30\,(1 - \frac{30}{144})$$

$$K = \frac{5}{30}\,(1 - \frac{30}{144})^{-1} = 0.211 \text{ watt/deg.}$$

Using this value of K results in

$$Y = \frac{K}{2K_t} = \frac{0.211}{2 \times 2 \times 10^{-2}} = 5.28 \text{ cm.}$$

then $$R_i = \frac{\rho}{Y} = \frac{0.89 \times 10^{-6}}{5.28} = 0.172 \times 10^{-3}$$

and $$I_{\varphi} = \frac{ST_c}{R_i}\,\frac{\Delta T}{\Delta T_m} \cdot A$$

$$= \frac{400 \times 10^{-6} \times 268}{0.172 \times 10^{-3}} \cdot \frac{30}{144} \cdot I$$

$$= 130 \text{ amps}$$

which is nearly the same as obtained for the cooler with optimized cooling capacity (133 amps). This is to be expected because in Chapter II, it was shown that the ratio of $\frac{\Delta T}{\Delta T_m}$ is very nearly the ratio of corresponding quantities for the two types of operation - maximum cooling and maximum coefficient of performance. Since the optimum coefficient of performance is about $\frac{\Delta T_m}{\Delta T}$ times the value of coefficient of performance occurring when cooling capacity was optimized. Whereas, the value of R_i has decreased in the ratio of $\frac{\Delta T}{\Delta T_m}$, one should have the same values of current to give the given output of 5 watts.

Dimensions of the Cooler: As discussed in the previous design, the criterion for choosing the dimensions of the cooler is the contact resistance. Allowing in all a 10 per cent decrease in the figure of merit and assuming that 8 per cent decrease is due to the cold junction resistance, it was found that the minimum length of arm should be 0.516 cm. In the design of the cooler, with optimized coefficient of performance, this limit will hold. Thus

$$l = 0.516 \text{ cm.}$$

$$\therefore \text{area of cross section} = Y\,l$$

$$= 3.95 \times 516$$

$$= 2.04 \text{ cm}^2 .$$

Total volume of thermoelectric material

$$2 \times a\,l = 2 \times 2.04 \times 0.516$$

$$= 2.11 \text{ cm}^3.$$

CHAPTER IV

DESIGN AND CONSTRUCTION OF AN EXPERIMENTAL COOLER

Selection of Geometry

In the previous chapter it was shown that for the given design conditions and from practical consideration of junction resistance the thermoelements could be as short as 0.516 cm. The cross sectional area of each element of the cooler designed on maximum cooling capacity basis (most compact cooler using minimum material) was 0.568 cm^2 whereas for the cooler designed on maximum COP (most efficient cooler requiring least input power) the elements section was 2.04 cm^2. It may be realized that these two designs are for some particular situations where either the space occupied by the device or the power consumption is the most important consideration. Desired dimensions of the elements can be obtained by cutting suitable lengths from a sample and machining them to required sizes. Machining can be accomplished by acid cutting, by hand sawing or by hand sanding.

Machining and cutting of semiconductor materials like lead telluride is a very delicate operation. For an experimental cooler, neither of the designs worked out in Chapter III was suitable as elements of those particular dimensions were not available from the manufacturing firms. In order to avoid any machining or cutting of the material, elements of lead telluride having 1/2" length x 1/2" diameter, which is one of the standard sizes of TEG #2 elements supplied by Minnesota Mining and Manufacturing Company, were used in the experimental cooler.

Electrodes

In accordance with the nomenclature adopted in other published literature on thermoelectric devices, the term electrode used in this text designates any material of high conductivity placed in contact with the end of a thermoelement.

Selection of electrode material: According to Fritts (19), a suitable electrode must fulfill the following requirements:

1. The electrode must provide the principal mechanical support for thermoelements.
2. The electrode must furnish good electrical conductance through the thermoelectric system and must not introduce any significant resistive component compared to the volume resistance of the elements.
3. The electrodes additionally must provide good heat transfer into and out of the thermoelectric junctions.

Apart from the above requirements, which are of physical nature, the following considerations, which are of chemical nature, are very important.

1. The electrode material must be chemically stable in contact with the thermoelements under operating conditions.
2. The formation of a junction must not result in the creation of an intermediate layer of high resistivity.
3. Where a physical bond is created by solder or other means, the electrode and thermoelement must have well-matched thermal

expansion coefficient. The interdiffusion of thermoelement and electrode should not create a physically weak phase within the plane of the junction.

4. Where a solder bonded electrode is formed satisfying all the above conditions, care should be taken to insure that the solder does not act as a diffusion vehicle which may deposit poisoning material on the thermoelement.
5. The electrode material should not alloy with thermoelement, not diffuse with the thermoelement and not react directly with the thermoelectric alloy to destroy its molecular form. The electrode material should not dissolve a doping agent to effectively leach it out of the thermoelement.

Electrode material for use with PbTe alloys: In view of their chemical reaction Cu, Zn and Cd are not suitable for electrodes in PbTe systems. Iron and iron alloys are well suited for use with both P and N type PbTe because of the chemical stability between these two systems in contact with each other. The use of iron alloys with PbTe elements is described in U. S. Patent No. 2,811,569. Pure iron and PbTe react at quite elevated temperatures to form an eutectic mixture which solidifies at 1615^{o}F or only 73^{o}F below the melting point of pure PbTe. Iron, when present as a trace impurity in PbTe alloys, acts as an inert gradient and does not dope the crystal as do many other metals.

Stainless steel or other high alloy steel is not suitable for use with PbTe as the alloying agent may react with the element. Stainless steel with substantial chromium content tends to form protective films of Cr_2O_3 in the presence of traces of oxygen and water vapor. Unlike oxide of iron, Cr_2O_3 cannot be reduced as carbon or hydrogen at the hot junction operating temperature.

The electrodes used as hot and cold junctions for the experimental cooler are of common cold rolled steel with low alloys.

Joining Techniques

Joining the thermo-elements to hot and cold junctions is the most difficult job in assembling the device. As discussed in previous chapters, the resistances of the joints have to be very, very small, rather negligible in comparison to the resistance of the elements. The author of this study went through quite a good amount of literature on this subject before attempting to assemble the experimental cooler.

There are two methods of forming the junctions: (1) diffusion bonding or pressure contacting, and (2) soldering. In the following lines these junction forming techniques and associated problems are discussed in detail. Most of the information gathered has been taken from 3M Company's literature written by Fritts (19).

Pressure contacting: The contact is formed by placing the machined surface of the thermoelement against the electrode under light pressure (about 100 Psi). When heated to elevated temperature, the PbTe flows under compressive loading to seat intimately upon the iron surface. If the two surfaces of the pressure contact are oxidized before assembling the initial contact resistance (measured at room temperature) will appear quite high until the junction is heated above 700^{o}F whereupon the oxide film is destroyed by absorption or by volatilization of the oxide complexes.

The pressure type contact at hot junction is the most suitable design for thermoelectric generators with PbTe alloys. Contact resistances comparable with those obtained with good soldered electrodes can be obtained with PbTe ingots pressed against iron under reducing (or nonoxidizing) conditions at temperatures above about 700°F. Below this temperature, pressure contacts are not recommended by the manufacturers.

Soldering: Soldered junctions are well suited for both hot and cold junctions in a cooling device. The problem is that of selecting the type of solder and method of soldering which would give the best results. Type of solder -- generally speaking, solder should be of high conductivity, extremely thin and must not soften at any temperature near the working range. It should also have a thermal expansion coefficient intermediate between that of junction material and the semi-conductor. In their literature 3M Company says that tin metal can be used with both P type and N type PbTe to provide negligible contact resistance. The tin, however, must be applied to a PbTe surface free from surface oxides if a satisfactory contact is to be obtained.

It is reported by some authors that for lower temperature range of refrigerators solder with indium or bismuth as a base have proved quite satisfactory. Justi (20) mentions that a solder with 50% tin and 50% indium proved very successful for use in cooling devices. Shilliday (21) reports that good results were obtained by plating the junctions with rhodium and using ordinary solder. Kaye and Saldi (22) have reported that for their experimental cooler indium-tin proved to be the best. Method of soldering -- Many soldering methods were adopted in different laboratories and the results were compared. Kaye and Saldi (22) report that they tried the following methods for the experimental cooler based on Bi_2Te_3 elements:

a) Inert soldering gun: A special soldering gun was used in which argon was heated and applied to protect the surfaces of the element from oxidation.

b) Crucible method: After carefully sand blasting with S. S. White Company's No. 1 abrasive powder, the surfaces were nickel plated to a thickness of 0.001 inch, thus yielding nonoxidizing surface which was more wettable to solder than the element surface. The prepared surfaces were then dipped into ordinary molten solder at 460°F for five seconds, removed and excess solder wiped out. But the solder temperature of 460°F caused the end of the P-type leg at the junction with copper bridge to change to N type.

c) Ultrasonic soldering: After the surface to be soldered was cleaned and nickel plated, the element was heated on a hot plate, set at 175°C and indium tin solder was melted on the clean surface with the hot tip of ultrasonic soldering iron. Good junctions were not obtained with this method. The only advantage of this method is that when the molten solder is applied with an ultrasonic soldering device, the surface oxide which is under the protection of molten solder is mechanically disrupted.

d) Nonacid flux soldering: The surfaces were sand blasted and nickel plated. A nonacid flux was placed on the surface and heat was applied with a weller soldering gun. As the flux started to boil, indium-tin solder was applied and spread evenly with the gun. This method was proved to be most successful.

Joining procedure adopted in the experimental cooler: The PbTe elements supplied by 3M Company were pretinned at one end which was supposed to be joined in the cold junction. These elements which perhaps were primarily meant for thermoelectric generators were not tinned at the other end which was to be joined to the electrode by pressure contact method. Many solders, i.e. soft tin, tin bismuth and tin indium and various nonoxidizing fluxes, were used while trying to join the untinned surface to the electrode, but the element surface did not wet at all. In these attempts, one set of elements was cracked (probably due to prolonged heating). The elements were sent to the supplier (3M Company) who kindly agreed to pretin the other ends, too. With their pretinned surfaces, it was possible to solder these elements to iron alloy electrodes. Tin indium solder proved to be much better than other types (soft tin, lead, and tin bismuth) and was used in final assembly. This solder consists of 50% tin and 50% indium, with a melting point of 138°C, has high electrical conductivity, good wetting properties and low melting point, but does not soften in the working range of the device.

The electrode surface was cleaned and nonoxidizing soldering paste was spread on the electrode surface. Heat was applied with a weller soldering gun. When the flux started to boil, indium-tin solder was applied and spread. Then the element was placed on the electrode with light pressure. Now heat was applied not on that side of the electrode in contact with the element, but from the other side, care being taken that the heat reaching the joint was just enough to melt the solder. When the solder started melting and the element was seated properly heat was removed. Light pressure was continued to be applied on the element until the solder solidified. In this way, first both the elements were soldered to the cold junction and then to the hot one. After several attempts, all of the four soldered junctions came out to be tolerably good.

Construction Details of the Experimental Cooler

Figure 11 shows the construction details of the experimental cooler and Figure 12 is a photograph of the final assembly. The device is based on single elements of 1/2" diameter x 1/2" length P and N type lead telluride elements TEG #2 manufactured by Minnesota Mining and Manufacturing Company. Both cold and hot junctions are made of low alloy steel. The cold junction is 2 1/2" long with 1" x 1/2" section at ends and 1" x 1" section in the middle. A hole is provided in the center of the cold junction where water drop can be placed and also thermocouple wires were soldered there. The hot junction consists of two fin assemblies, one at each side. Each fin assembly has an upper plate 4" x 4" x 1/4" thick and is electrically and mechanically connected with three lower plates 4" x 4" x 1/8" thick by means of four through bolts. Terminals for supply are provided in the upper hot plates and thermocouple wire is soldered to one of the plates. The entire unit is mounted on an insulated base 12" x 6" x 3/4" thick.

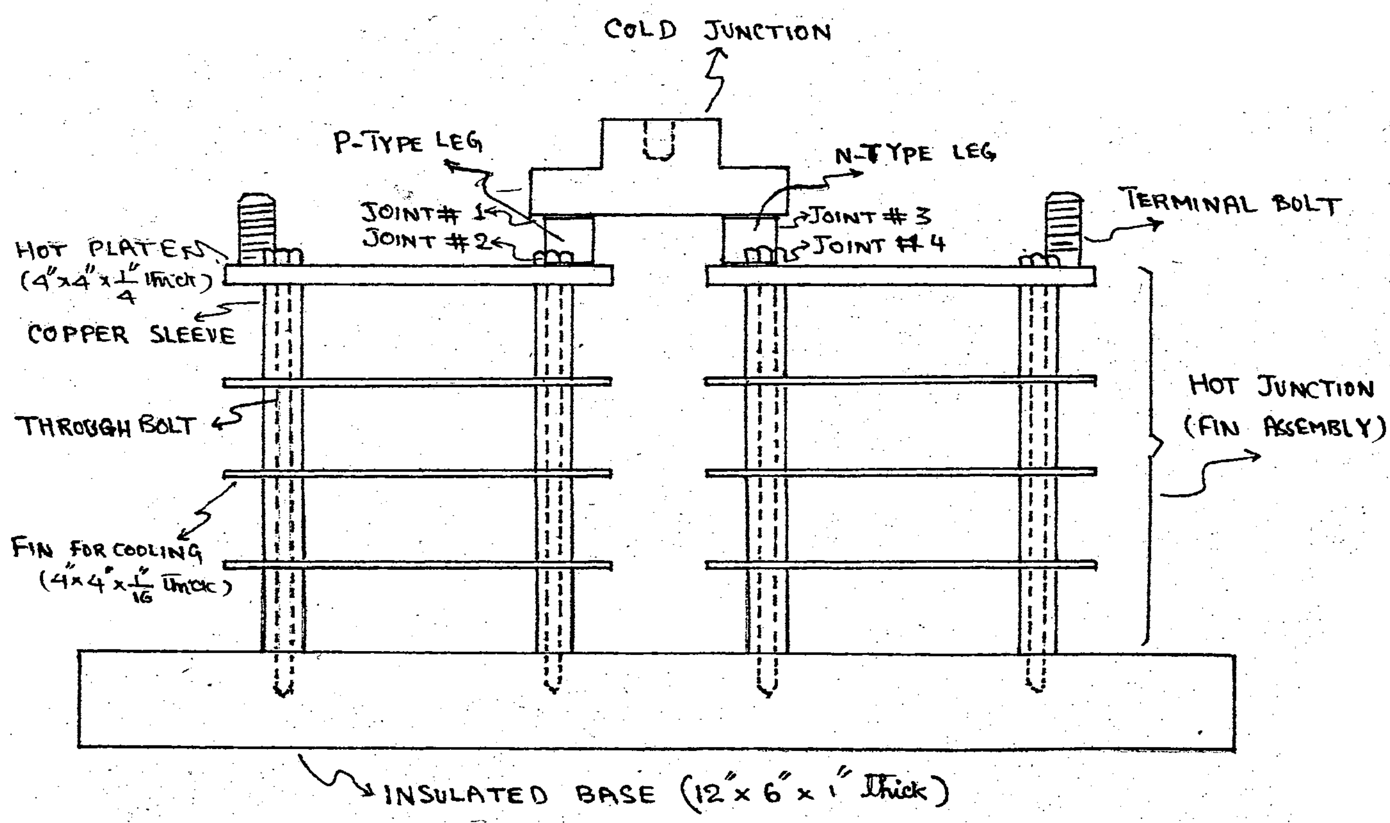


Figure 11. Construction Details of Experimental Cooler

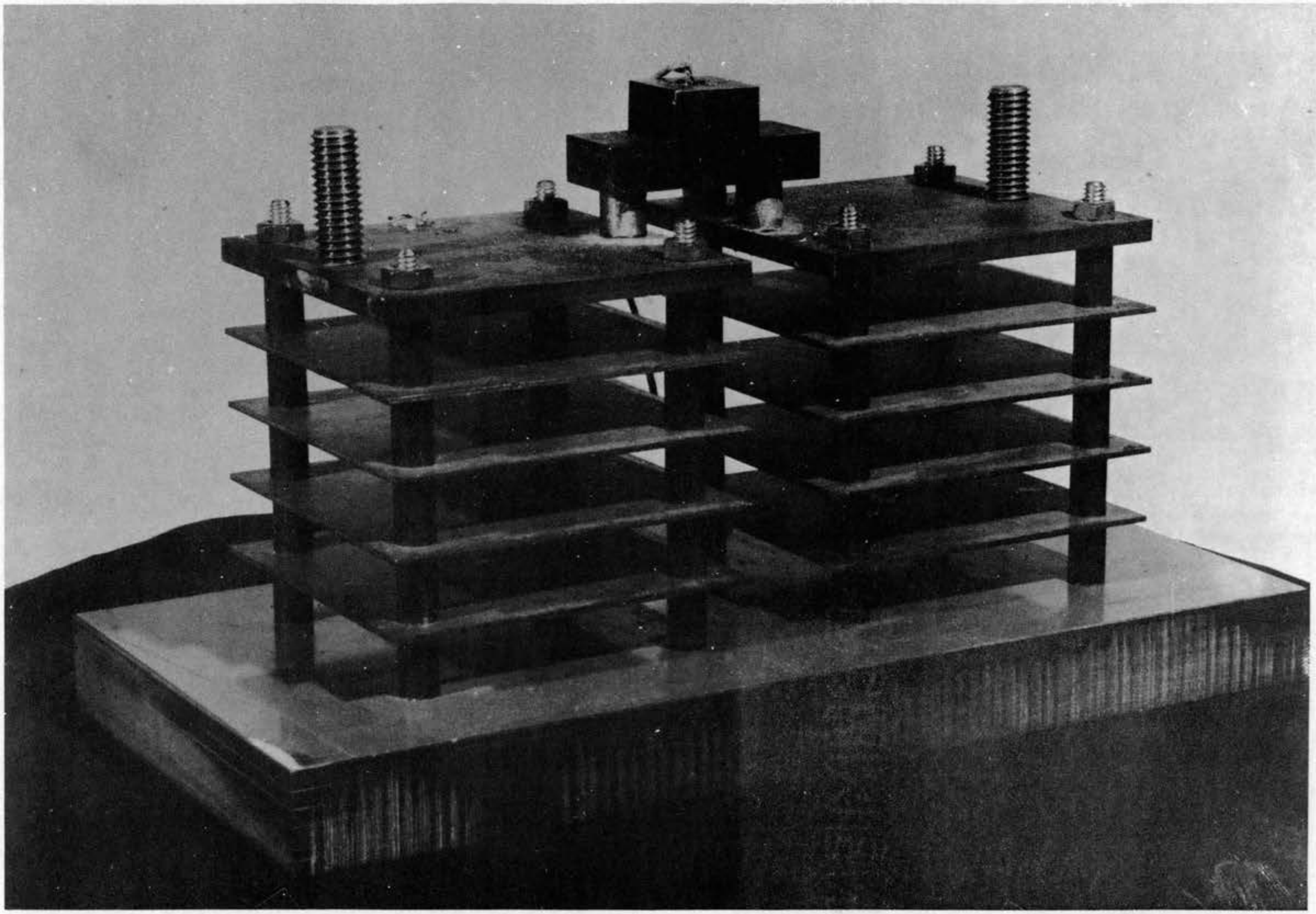


Figure 12. Photograph of the Experimental Cooler

CHAPTER V

PERFORMANCE OF THE EXPERIMENTAL COOLER

Data and Parameters

Temperature of cold junction . . . . – 5°C

Temperature difference between cold and hot junctions . . . . 30°C

	P type	N type
Seebeck coefficient	200 microvolts/°C	-200 microvolts/°C
Electrical resistivity	382×10^{-6} ohm cm	508×10^{-6} ohm cm
Thermal conductivity	0.02 watts/cm°C	0.02 watts/cm°C
Length of leg	½ inch (1.27 cm)	½ inch (1.27 cm)
Diameter of leg	½ inch (1.27 cm)	½ inch (1.27 cm)

Calculations for Theoretical Performance

$$Z = \left[\frac{/S_p/ + /S_n/}{\sqrt{K_p \rho_p} + \sqrt{K_n \rho_n}}\right]^2$$

$$= \left[\frac{200 \times 10^{-6} + 200 \times 10^{-6}}{\sqrt{2 \times 10^{-2} \times 382 \times 10^{-6}} + \sqrt{2 \times 10^{-2} \times 508 \times 10^{-6}}}\right]^2$$

$$= \left[\frac{400 \times 10^{-6}}{\sqrt{764 \times 10^{-8}} + \sqrt{1016 \times 10^{-8}}}\right]^2$$

$$= \left[\frac{400 \times 10^{-6}}{27.7 \times 10^{-4} + 31.8 \times 10^{-4}}\right]^2$$

$$= \left[\frac{400 \times 10^{-6}}{59.5 \times 10^{-4}}\right]^2$$

$$= 4.55 \times 10^{-3} \ \text{deg}^{-1} .$$

In these calculations, the junction resistance and copper lead resistances are neglected.

For the given geometry:

$$Y = \frac{\text{area}}{\text{length}} \quad \text{factor} = \frac{\frac{\pi}{4}(\frac{1}{2})^2}{\frac{1}{2}} = \frac{\pi \times 2}{16} \text{ inch}$$

$$= \frac{\pi \times 2}{16} \times 2.54 \text{ cm.} = 1 \text{ cm}$$

$$R_i = R_p + R_n$$

$$= \frac{\rho_p l_p}{A_p} + \frac{\rho_n l_n}{A_n}$$

but since $\frac{l}{A} = 1$ for both, the following is obtained:

$$R_i = 382 \times 10^{-6} + 508 \times 10^{-6}$$

$$= 890 \times 10^{-6} \text{ ohm.}$$

Theoretical maximum COP (based on Carot cycle):

$$= \frac{T_c}{T_h - T_c} = \frac{263}{30} = 8.93.$$

$$\text{Maximum COP} = \frac{T_h}{T_h - T_c} \cdot \frac{\sqrt{1 + \frac{Z}{2}(T_h + T_c)} - \frac{T_h}{T_c}}{\sqrt{1 + \frac{Z}{2}(T_h + T_c)} + 1}$$

$$= 8.93 \cdot \frac{\sqrt{1 + \frac{4.55}{2} \times 10^{-6} (298 + 268)} - \frac{298}{268}}{\sqrt{1 + \frac{4.55}{2} \times 10^{-6} (298 + 268)} + 1}$$

$$= 8.93 \ \frac{\sqrt{1 + 2.775 \times 10^{-6} \times 566} - 1.11}{\sqrt{1 + 2.775 \times 10^{-6} \times 566} + 1}$$

$$= 8.93 \ \frac{\sqrt{1 + 1.534} - 1.11}{\sqrt{1 + 1.534} + 1}$$

$$= 8.93 \ \frac{1.59 - 1.11}{1.59 + 1}$$

$$= 1.67 \ .$$

Maximum temperature difference $(T_h - T_c)_{max}$

$$= \tfrac{1}{2} Z T_c^{\,2} = \tfrac{1}{2} \times 4.55 \times 10^{-3} (268)^2 = 163°C.$$

Minimum cold temperature

$$= \frac{-1 + \sqrt{1 + 2Z\,T_h}}{Z}$$

$$= \frac{-1 + \sqrt{1 + 2 \times 4.55 \times 10^{-3} \times 298}}{4.55 \times 10^{-3}}$$

$$= \frac{-1 + \sqrt{1 + 2.68}}{4.55 \times 10^{-3}}$$

$$= \frac{-1 + 1.91}{4.55 \times 10^{3}} = 200°K \text{ or } -73°C.$$

(Note: The maximum temperature difference and minimum cold temperature calculated on the previous page are only of theoretical interest. These are obtained when the cold junction is perfectly insulated from hot junction; and, hence, these are for zero COP).

$$I_{optimum} = \left\{ \frac{/S_p/ + /S_n/}{R_i} \right\} T_c$$

$$= \frac{400 \times 10^{-6} \times 268}{890 \times 10^{-6}} = 121 \text{ amps}$$

V = voltage drop across cooler

$$= IR + S\,(T_h - T_c)$$

$$= 121 \times 890 \times 10^{-6} + 400 \times 10^{-6} \times 30$$

$$= 0.108 + 0.012 = 0.12 \text{ volts.}$$

Q_p = Rate of heat transfer due to Peltier effect

$$= ST_c \times I$$

$$= 400 \times 10^{-6} \times 268 \times 121$$

$$= 13.0 \text{ watts.}$$

Q_j = Rate heat loss due to Joule effect

$$= \tfrac{1}{2}\, I^2 R_i$$

$$= \tfrac{1}{2}\,(121)^2 \cdot 890 \times 10^{-6}$$

$$= 6.5 \text{ watts.}$$

Q_{cond} = Rate of heat loss due to conductance

$$= (T_h - T_c)(K_p \frac{A_p}{L_p} + K_n \frac{A_n}{L_n})$$

$$= 30\ (0.02 + 0.02)$$

$$= 1.2 \text{ watts.}$$

Q_{net} = net rate of heat transfer

$$= Q_p - Q_j - Q_{cond}$$

$$= 13.0 - 6.5 - 1.2$$

$$= 5.3 \text{ watts.}$$

Power = V x I = 0.12 x 121 = 14.52 watts

$$\text{COP} = \frac{Q_{net}}{\text{Power}} = \frac{5.3}{14.52} = 0.366.$$

Comparison of Designs

In Chapter III, two designs of a thermoelectric cooler were presented. These two designs were based on two different objectives; one approach was for designing the most compact cooler (maximum cooling capacity) and the other for designing the most efficient device (maximum COP). In Chapter IV, an experimental cooler was designed from the point of view of ease in construction. The performance of these three different designs are also calculated in the previous pages. The basic features of these designs are compared in Table I on page 55.

TABLE I

COMPARISON OF DESIGNS

Requirements: Heat load. 5 watts
Cold junction temperature. . . . . $-5^{o}C$
Hot junction temperature . . . . $25^{o}C$

Material Used: Lead telluride thermoelements TEG #2 of 3M Company.

Seebeck coefficient $(S = /S_n/ + /S_p/) = 400$ micro volt/^{o}K

Electrical resistivity $(\rho_p) = 0.382 \times 10^{-3}$ ohm-cm
$(\rho_n) = 0.508 \times 10^{-3}$ ohm-cm

Thermal conductivity $(K_p = K_n) = 2 \times 10^{-2}$ watt/cm/^{o}C

	Design Based on Max. Cooling Capacity	Design Based on Maximum COP	Experimental Model
Coefficient of Performance	0.355	1.29	0.366
Thermal Conductivity (w/deg)	0.044	0.158	0.102
Area/Length Factor (cm)	1.1	3.95	1
Length of Elements (cm)	0.516	0.516	1.27
Cross Section Area of Elements (cm^2)	0.568	2.04	2.54
Electrical Resistance (ohm)	0.808×10^{-3}	0.225×10^{-3}	0.89×10^{-3}
Optimum Current (amps)	133	116	121
Volume of elements (cm^3)	0.585	2.11	3.22
Heat pumping capacity (watts)	5	5	5.3

Experimental Setup

The experiments with the cooler were conducted in the laboratory room which was somewhat overheated. The average room temperature during the experiments was 35.5°C. The hot junction was kept at room temperature. A circulating air fan placed near the fin assembly supplied moving air to the hot junction to maintain it at nearly constant temperature. It was not possible to place the fin assembly in a water bath because the upper plates which were in the electrical circuit were also connected with the rest of the assembly as no insulation was provided in the through bolts. The cold junction was insulated by wrapping it with cotton and sterofoam packing. A drop of water was placed in the hole at the center of cold junction.

Steady direct current was passed through the cooler and temperatures of cold and hot junctions were measured at intervals of five minutes until the cold junction temperature became constant and did not decrease any more. The temperature difference - time transients - were obtained for direct currents of 5, 10, 15, ..., 50 amps. For supplying currents up to 25 amps, exide batteries were used; and for higher currents, rectifier was used as source of power supply. The rectifier supplied full wave rectification and was used with filtering arrangement to reduce ripple. However, it is estimated that there was about 10% or slightly more ripple present.

The temperatures of cold and hot junctions were measured by thermocouple wires soldered to these junctions during the assembly of the cooler. The thermocouple wires were soldered to the cold junction inside the central hole and to the hot junction at the upper plate of one

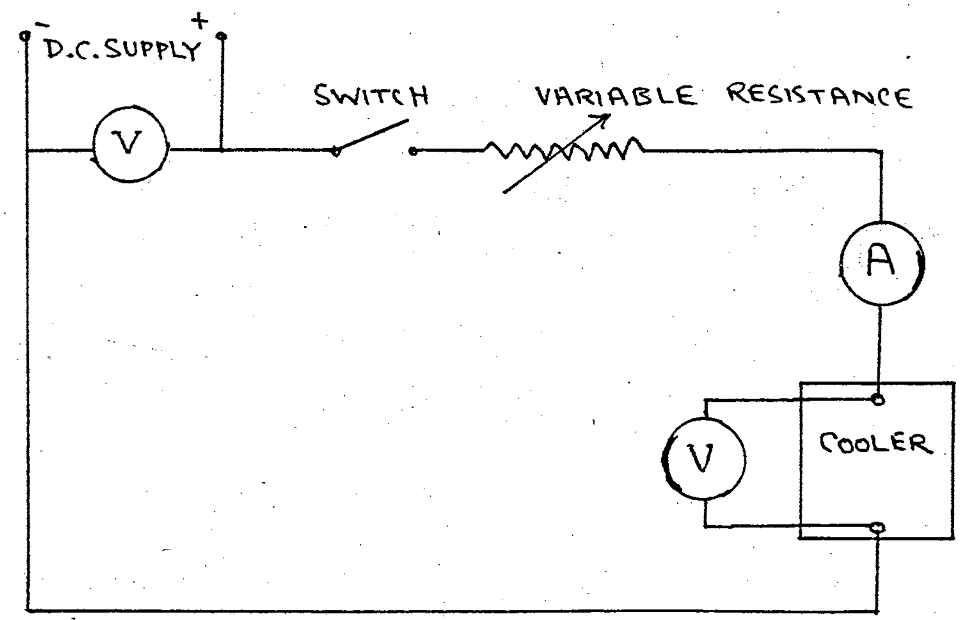


Figure 13. Diagram of Experimental Setup

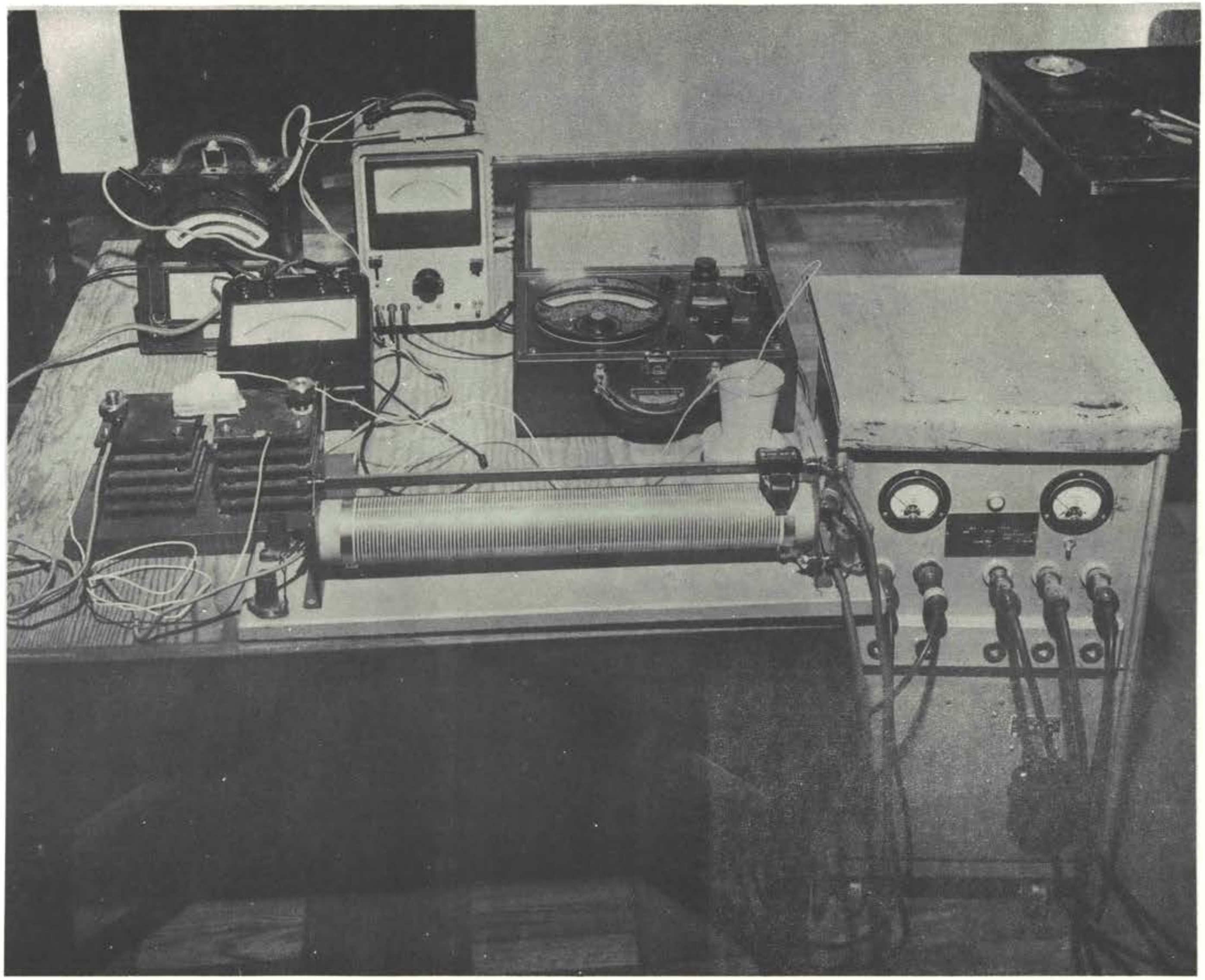


Figure 14. Photograph of the Experimental Setup

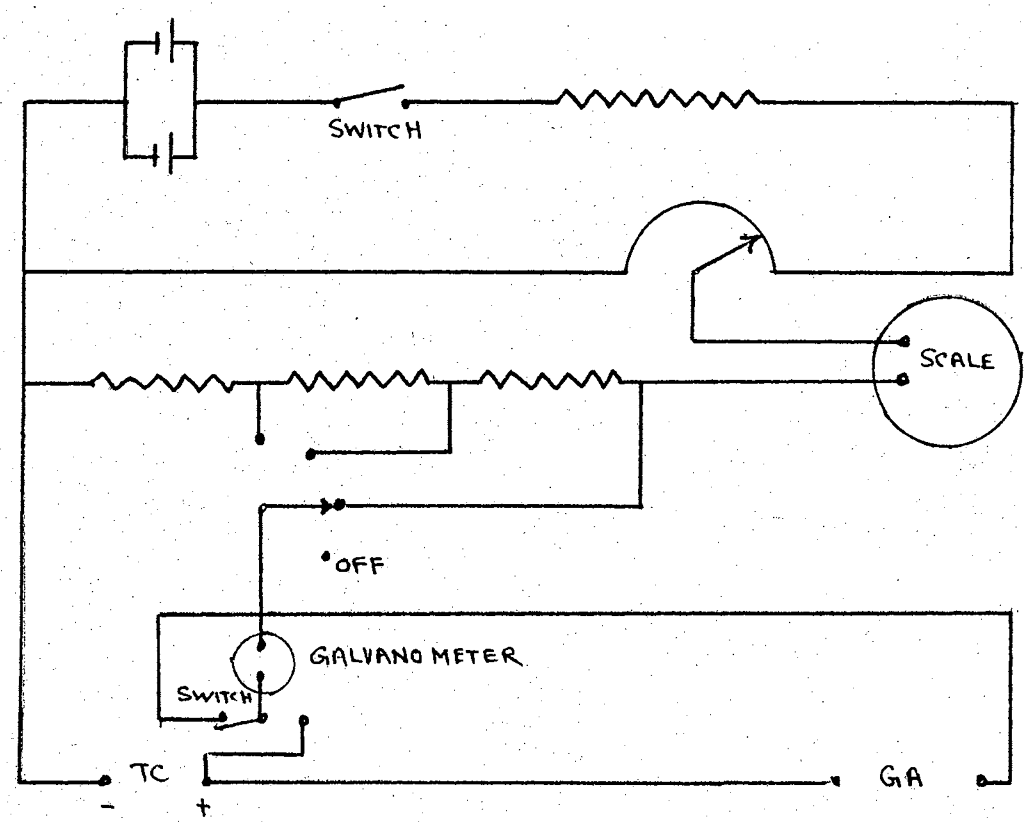
of the fin assemblies. General Electric high accuracy copper-copnic wires (24 AWG) were used as thermocouple wires and temperature was measured by means of G. E. thermocouple potentiometer type PJ-84. The connection diagram and temperature measurement arrangement is shown in Figure 15. Melting ice was used as cold reference while measuring the temperatures.

Experimental Results

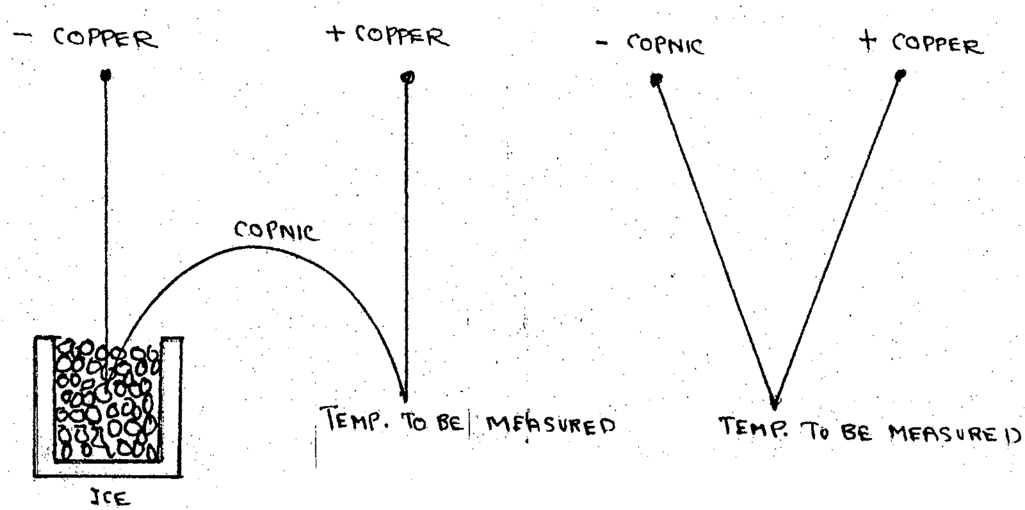
The contact resistance of the four junctions could not be measured accurately as there was no suitable apparatus for measuring such low resistances. With the bridge arrangement and ammeter-voltmeter method, it was revealed that there was no detectable change in the system resistance measured before and after assembly of the cooler. However, during the experiments with the cooler it was found that joint No. 4 was much worse as the hot junction plate adjoining it was heated up appreciably. The voltage drop across this plate was also higher than it should have been.

Contact resistance measuring apparatus: An apparatus (Figure 16) devised for the measurement of contact resistance has been described by R. W. Fritts of 3M Company. By this apparatus, the voltage drop across a contact into the body of the thermoelement is traced. Contact resistance or presence of any cracks will be indicated by the plot of voltage drop. It is claimed that contact resistances as low as $10^{-5}\ \frac{\text{ohm}}{\text{area}}\ \text{inch}^2$ can be measured by this apparatus.

The experimental data are shown in Figures 17 and 18. For each value of steady current, temperature difference-time transients have



(a) Potentiometer Circuit (G. E. Thermopile Potentiometer Type PJ-84)



(b) Temperature With Reference To Ice

(c) Temperature With Reference to Room Temperature

Figure 15. Arrangement for Temperature Measurement

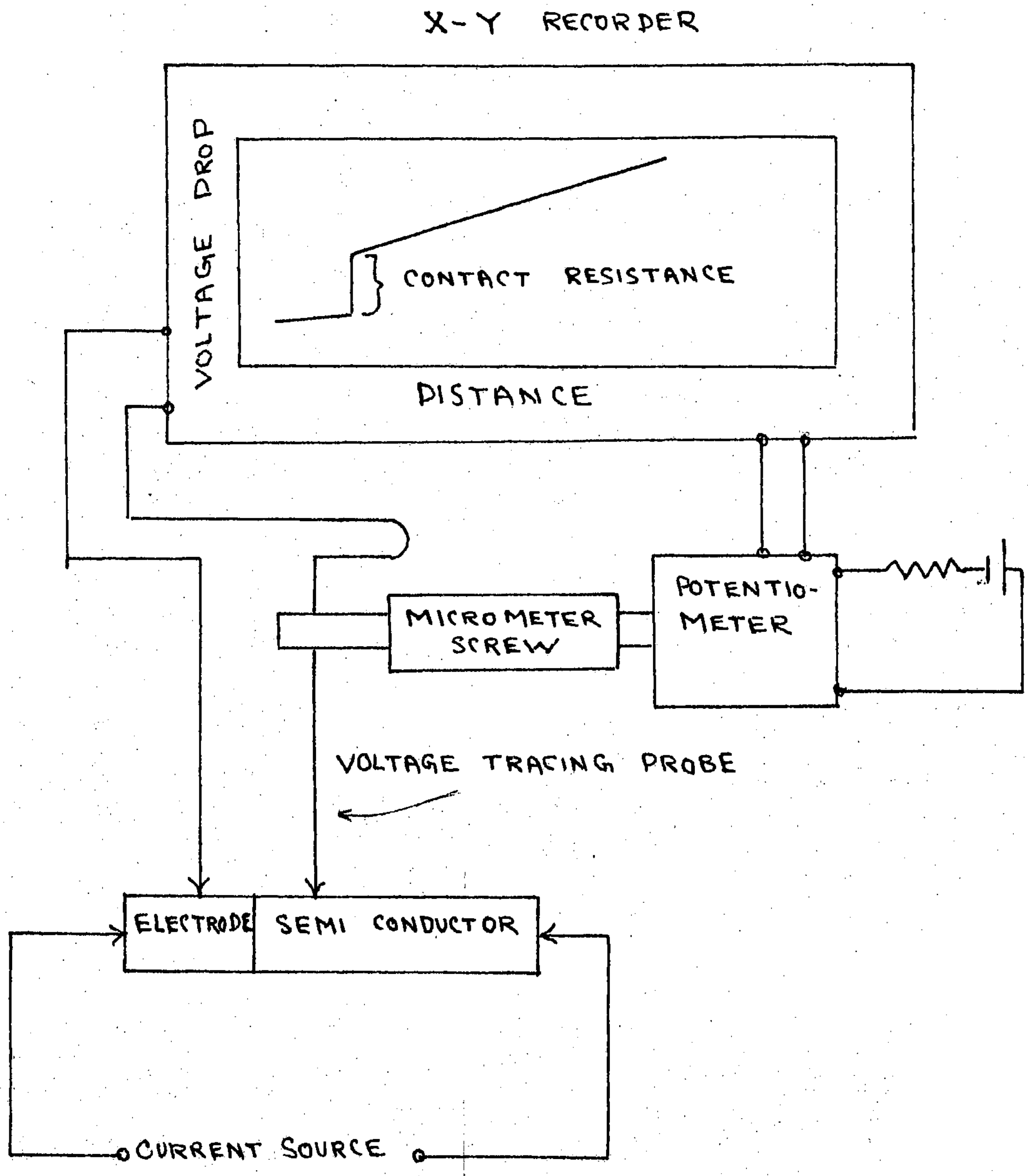


Figure 16. Contact Resistance Measuring Apparatus

been drawn in Figure 17. It was observed that after a certain time the temperature of cold junction became steady. During the experiments a maximum increase in hot junction temperature was observed to be 2°C. A graph showing maximum temperature difference versus current is drawn on Figure 18 from the transient curves by cross plotting asymptote values of temperature difference for each value of current. The COP calculated from measured data is also plotted on Figure 18.

Remarks on Experimental Results

For the sake of comparison, theoretical values of temperature difference and COP as functions of current are also plotted on Figure 18. It may be noted that the measured values are much lower than the theoretical ones. Theoretical calculations had shown that optimum current for maximum temperature difference was 121 amps. This is very large current and to supply this current at low voltage was a great practical difficulty. In the laboratory tests currents up to only 50 amps were passed through the device, so the device could not be tested for its entire range of operation. However, it gave temperature difference up to 15.5°C. In Figure 18, the curve of temperature difference versus current was hypothetically extended for higher values of current. The extended curve was drawn by approximations and back calculations assuming a certain value for resistance of junctions, hot and cold electrodes and leads as given by the measured data. Similarly the values of COP were also measured and hypothetically calculated for different values of current.

The disagreement between the theoretical and measured results can be attributed to the following reasons:

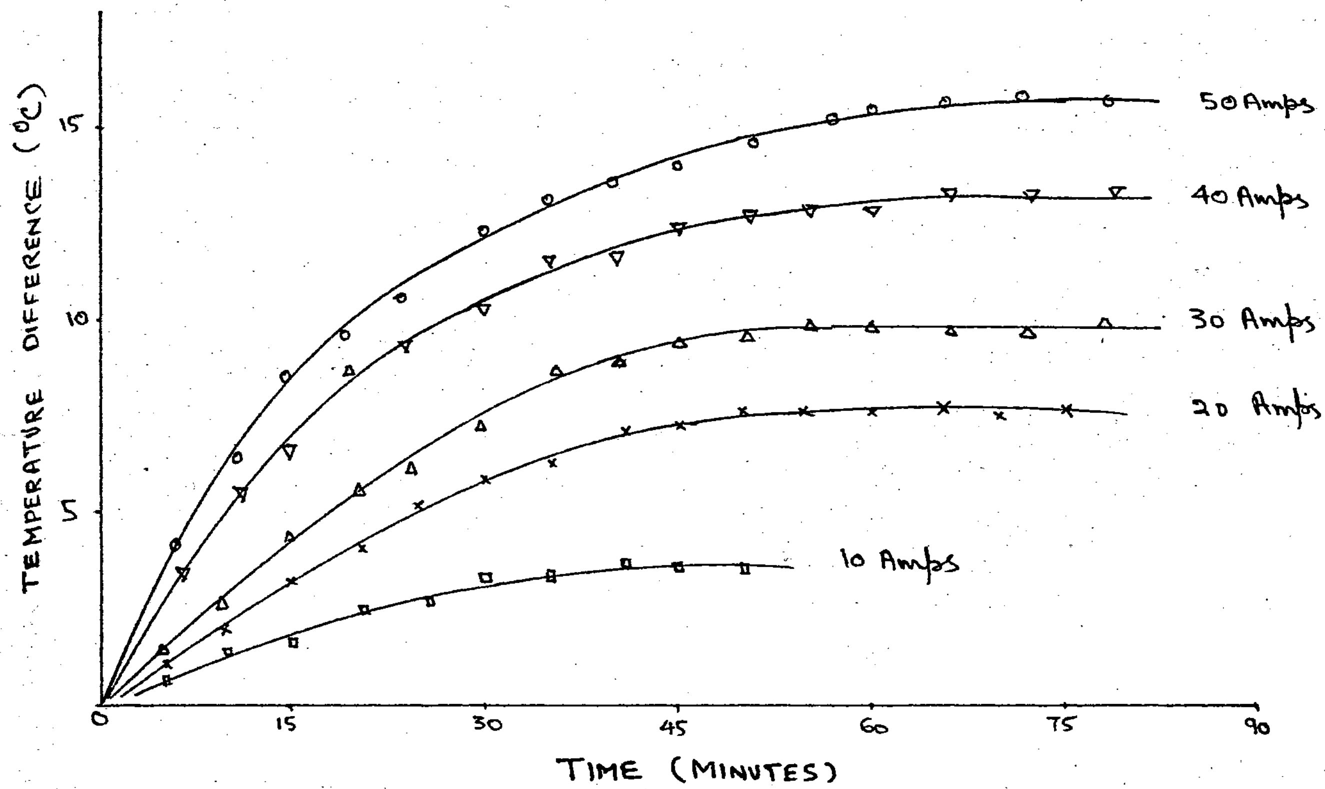


Figure 17. Temperature Difference-Time Curves

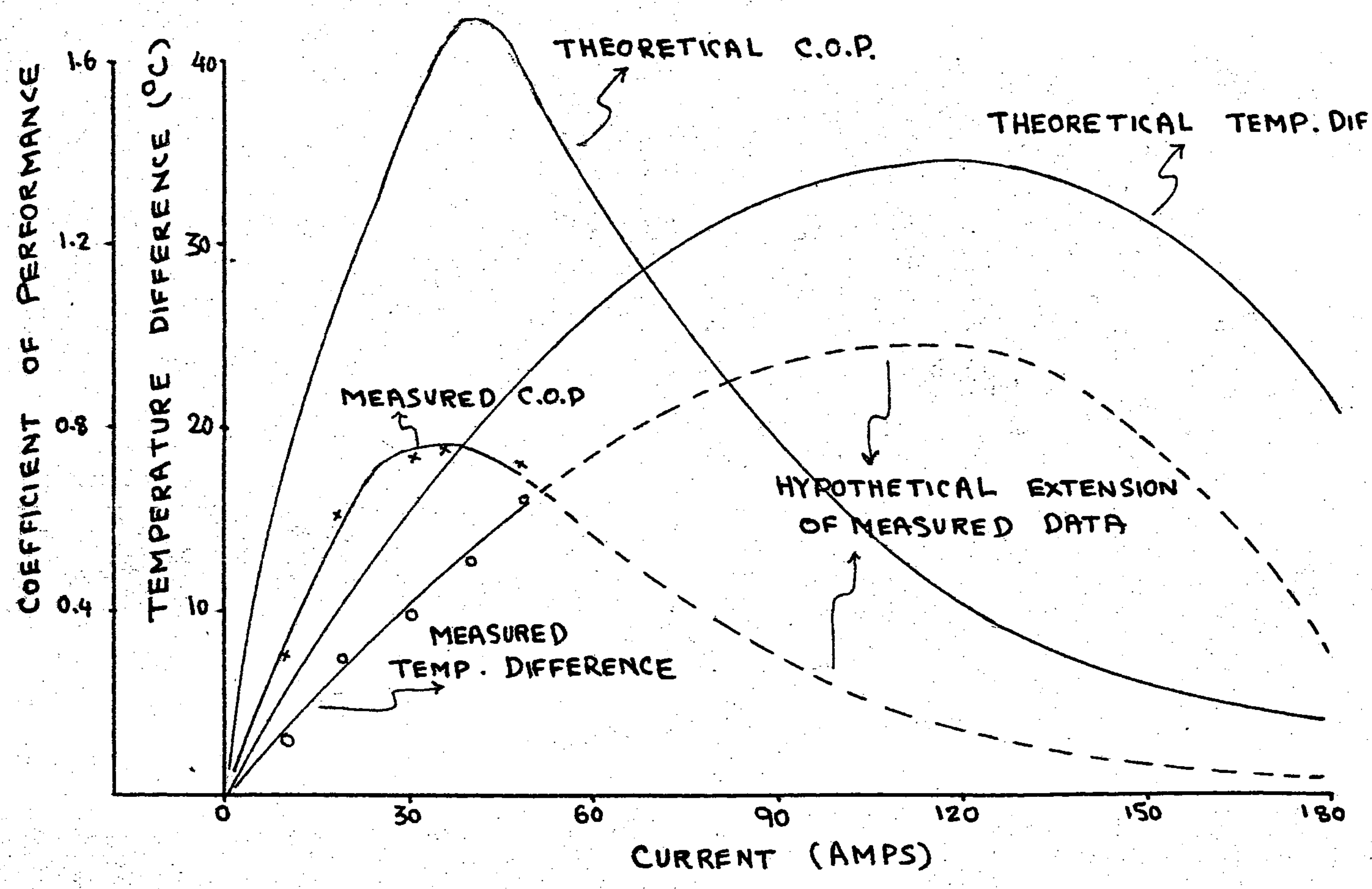


Figure 18. Temperature Difference, COP Versus Current Relationship

1) Theoretical calculations neglected junction resistance, as well as resistance of hot and cold electrodes and connecting leads. In the experiment, though the electrodes and leads resistances were low and did not matter much but the resistance of the four soldered junctions was not as low as it should have been. These junctions were far from being perfect.

2) In theoretical calculations it is assumed that hot junction is at constant temperature. In almost all the experimental models tested in the manufacturer's or research laboratories, the hot fin assembly was placed in a well stirred water bath in order to maintain a constant temperature hot junction. This could not be done in the experimental model here because, for ease in construction, no electrical insulation was provided in the through bolts joining the hot plates with the fin assembly. Hot junction and fin assembly dissipated heat in surrounding air and were kept at nearly constant temperature by means of a fan. However, a rise in temperature of 2°C was observed.

3) The power was supplied by means of batteries and also by rectifier. The battery did not supply a very constant voltage throughout the experiement and the current was to be adjusted by means of variable resistors. The rectifier on the other hand had some ripples which resulted in some loss in the coefficient of performance.

CHAPTER VI

SUMMARY AND CONCLUSIONS

Summary

The object of this thesis was to present the analysis of design, design calculations, criteria for selection of material, construction problems and procedures, performance calculations and experimental results of a single stage thermoelectric cooling device. History of development of thermoelectric cooling starting from the discovery of Seebeck and Peltier effects up to recent accomplishments is also briefly mentioned.

Mathematical analysis and calculations were presented for two ideal designs, one based on the optimum cooling capacity and the other on optimum coefficient of performance. A third design based on practical considerations was discussed and adopted for the experimental device constructed in the laboratory. Basic features of design and theoretical performance of these three coolers were compared. Mathematical analysis of design and performance disclosed many of the problems encountered in thermoelectric heat pumps. These problems occur in the selection of material, joining techniques and arranging for power supply. In this thesis special attention has been given to the joining problem which is by far the most difficult and delicate operation in the construction of semi-conductor devices.

An experimental cooling junction was constructed and tested to demonstrate the practicability of thermocouple as a heat pump without any moving parts. Soldered junctions had to have negligibly low contact resistance but such perfection could not be accomplished by continued trials due to the limitations in laboratory equipment and time at disposal. Again, this cooler, which theoretically required about 121 amps at 0.12 volts for maximum temperature difference, could not be tested in its entire range of operation due to practical difficulties in arranging such a high currents and low voltage supply. However, a temperature difference of 15.5°C and a maximum coefficient of performance of 0.8 was obtained with the experimental device.

Conclusions

The mathematical analysis of design and performance as well as the construction and test data of the experimental model have led to the following conclusions:

1) With the increasing knowledge of the properties of thermoelectric materials and the mathematical analysis to forecast the performance of a thermoelectric device, it is possible to design a cooling device to meet the desired requirements. Thermoelectric cooler has become a device for practical use and is much more than a laboratory curiosity.

2) Better thermoelectric materials can considerably improve the performance of a cooling device. The criterion for better materials is higher figure of merit. As the science of material development progresses thermoelectric devices will have wider and wider applications.

3) Lead telluride and its alloys, though they posses good figure of merit, are not well suited for use in cooling devices. The TEG #2 elements used in the experiment cooler were developed and manufactured by 3M Company, primarily for use in thermoelectric generators. The cooler based on these elements did give some degree of cooling capacity and COP, but at high currents. It is gathered from 3M Company that they have developed certain elements based on Bi_2Te_3 systems mainly for use in coolers. A heat pump based on similar design and construction features as those of the experimental cooler, but using Bi_eTe_3 elements would have given higher temperature difference with much lower currents.

4) Junction resistance is a limiting factor in designing a thermoelectric device. The design requirements do not determine the size of the elements or their volume but only the ratio of area to length of section. Theoretically there is no limit for decreasing the dimension of a cooler and economizing the material, but the limit is set by junction resistance. Advancement in techniques for joining semi-conductors will result in more efficient and more compact devices.

5) The inherent disadvantage of the thermoelectric cooler lies in the fact that they are high current and low voltage devices. This situation can be improved to a certain extent by adopting composite junctions or increasing the length of the elements, which involves higher cost for the material.

Though thermoelectric devices are technically feasible for a wide range of applications, the present situation calls for continued research in the science of development and fabrication techniques before these devices can become commercial product for day to day use.

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