THERMOELECTRIC REFRIGERATION

By

RUBEN A. GARCIA *

Introduction

Thermoelectric refrigeration uses DC electrical energy to achieve cooling directly. Conventional systems use either mechanical or heat as direct sources of energy. Thermoelectric effects were observed as early as the first half of the 19th century by Seebeck, Peltier, and Thomson.

Seebeck discovered that an electric current flowed in a closed circuit made of two dissimilar metals when the two junctions were maintained at different temperatures. He however failed to realize the significance of his discovery for he thought he had shown that magnetism was caused by a difference in temperature. Two years later, Peltier observed the inverse effect — the passage of electric current through the junction of two dissimilar materials resulted in either the absorption or evolution of heat at the junction. Peltier also misunderstood his discovery and moreover failed to recognize the relationship between his discovery and that of Peltier.

It took William Thomson to show the relationship between the Seebeck effect and Peltier effect by thermodynamic analysis. Thomson also discovered another thermoelectric phenomenon which became known as the Thomson effect.

Thermoelectric Effects

When electric current passes through a thermocouple whose junctions are at different temperatures, five thermoelectric phenomena take place. These are the Seebeck effect, the Peltier effect, the Joulean effect, the conduction effect and the Thomson effect.

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*Professor and Chairman, Department of Mechanical Engineering, College of Engineering, University of the Philippines.

Seebeck effect. For a small temperature difference between the two junctions of materials A and B, the open circuit voltage produced is proportional to the temperature difference. Thus, for Figure 1:

$$\Delta E_{SB} = \alpha_{AB}\Delta T \tag{1}$$

where

ΔE_{SB} = open circuit voltage

α_{AB} = Seebeck coefficient or thermoelectric power

= difference between the absolute Seebeck coefficients for materials A and B.

ΔT = temperature difference between junctions of materials A and B.

The Seebeck coefficient for metals is quite low, $\alpha \leqslant 0.00005$ volt/c and for semi-conductors it is typically between 0.0002 and 0.00025 volt/c.

Peltier effect. Using the same circuit but with a DC source added such as a battery as shown in Fig. 2, it has been found experimentally that the heat transfer rate 0 (evolved or absorbed) on either junction is proportional to the current I. Thus

$$Q = \phi_{AB} I \tag{3}$$

where ϕ_{AB} is the relative Peltier coefficient for materials A and B.

Kelvin showed in a thermodynamic analysis that

$$\phi_{AB} = \alpha_{AB} T \tag{4}$$

Thus

$$Q = \alpha_{AB} I\, T \tag{5}$$

where T is the absolute temperature of the junction

Joulean effect. Current flowing through a conductor with resistance R would result in an irreversible generation of heat called the Joulean effect. The magnitude is given by

$$Q_j = I^2 R \tag{6}$$

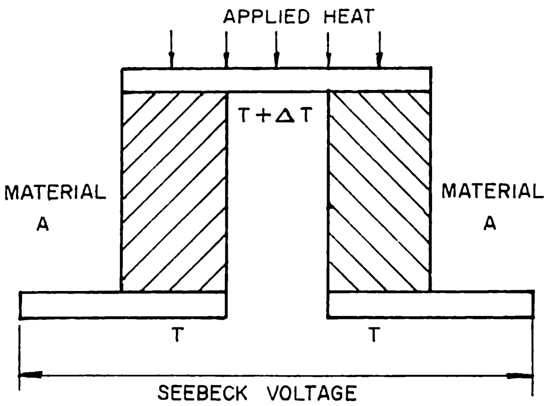

FIG. 1 SEEBECK EFFECT

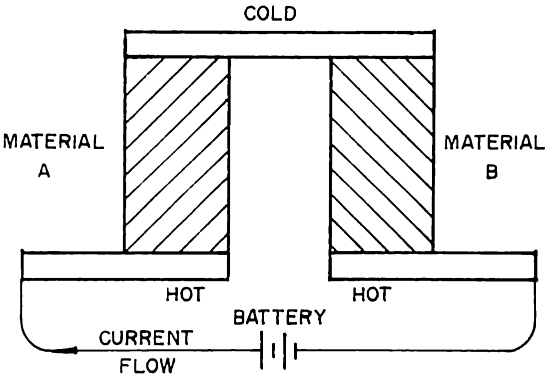

FIG. 2 PELTIER EFFECT

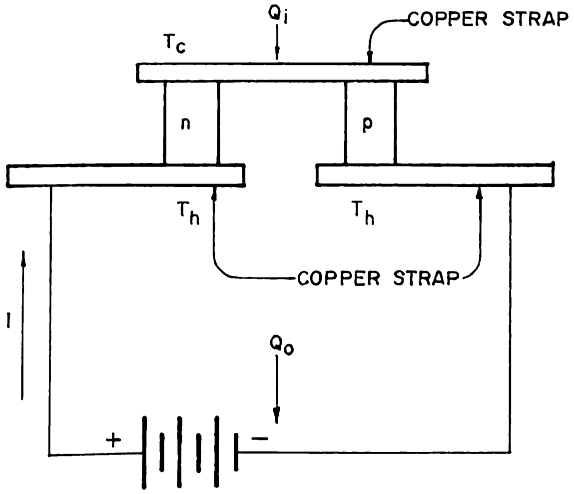

FIG. 3 PELTIER THERMOELECTRIC COUPLE

Conduction effect. When there is a temperature gradient between the junctions (see Fig. 3), heat will flow by conduction from the hot junction to the cold junction. This is called the conduction effect and may be expressed as

$$Qc = C\Delta T \tag{7}$$

where

C = the overall thermal conductance.

ΔT = $T_h - T_c$

Thomson effect. When current is passed through a thermocouple material in which a uniform temperature gradient initially exists, the temperature profile will be distorted in excess of the Joulean effect. The Thomson heat Q_T is given by

$$Q_T = \tau I \frac{dT}{dX}$$

where τ = Thomson Coefficient

dT/dX = temperature gradient along the thermocouple material.

Performance Analysis of Thermoelectric Couples

A circuit consisting of two dissimilar thermoelectric materials is referred to as a couple. With proper choice of materials the couple may be utilized for refrigeration purposes (see Figure 3). The n-type material has a negative Seebeck coefficient and an excess of electrons. The p-type has a positive Seebeck coefficient and a deficiency of electrons. There are a total of four connections between the thermoelectric materials and copper straps but there are only two thermoelectric junctions — the cold junction (upper) where heat Qi is absorbed at Tc and the hot junction (lower) where heat Qo is evolved. Reversing the current would interchange the cold and hot junctions. Assuming that:

(a) parameters α, p (resistivity), and k (thermal conductivity) of the materials are independent of temperature,

(b) heat exchange between the couple and its environment occurs only at the hot and cold junctions,

(c) electrical resistance of copper connecting strips is negligible, and

(d) one half (0.5) of the Joulean heat is transferred to each junction

we have for the cold junction, under steady-state conditions,

q

$$\alpha_{pn} I T_c = C\Delta T + 0.5\,(I^2 R) + Qi$$

or $$Qi = \alpha_{pn} T_c I - C\Delta T - 0.5\,(I^2 R) \tag{8}$$

Rewriting, we have $$\Delta T = (\alpha T_c I - 0.5 I^2 R - Qi)/C \tag{8a}$$

Similarly, for the hot junction,

$$Qo = \alpha_{pn} T_h I - C\Delta T + 0.5(I^2 R) \tag{9}$$

where α_{pn} = mean thermoelectric power in the temperature range from Tc to Th.

= $(\alpha p - \alpha n)$

C = effective thermal conductance between the two junctions

R = total electrical resistance (couple legs plus contact resistance at junctions) and the rest are as shown in Fig. 3.

The expression for the power input W can be determined from the energy balance on the system:

$$W + Qi = Qo$$

or $$W = \alpha pn\,\Delta\,TI + I^2 R$$

or $$W = (\alpha pn\,\Delta T + IR)I \tag{10}$$

Since $$W = VI; \quad V = (\alpha pn\,\Delta T + IR) \tag{11}$$

The coefficient of performance is

$$COP = \frac{Qi}{W} = \frac{\alpha pnTcI - C\Delta T - 0.5I^2 R}{\alpha\Delta TI + I^2 R} \tag{12}$$

This reduces to

$$\mathrm{COP} = \frac{Tc}{\Delta T} \quad \text{or} \quad \frac{Tc}{Th - Tc}$$

for a completely reversible thermoelectric system (no conduction and Joulean effects)

For maximum temperature difference and maximum refrigerating capacity we obtain

$$Iopt = \frac{\alpha pnTc}{R} \tag{14}$$

by equating to zero the first partial derivative of ΔT (equation 8a) with respect to I and solving for I.

Thus from equations (14) and (8a) the maximum temperature difference (Qi = 0)

$$\Delta T \max = 0.5\ ZT^2 c \tag{15}$$

and from equations (14) and (8), the maximum refrigerating capacity

$$Qi, \max = C[0.5ZT^2 e - \Delta T] \tag{16}$$

where
$$Z = \frac{\alpha^2}{CR} \tag{17}$$

The coefficient of performance at maximum refrigerating capacity can be found by equations (12) and (14):

$$\mathrm{COP}_{Qi,\max} = \frac{0.5ZT_c^2 - \Delta T}{Z^T hTc} \tag{18}$$

For maximum COP, the optimum current can be found by equating to zero the first partial derivative of equation (12) with respect to I and solving for I. Thus

$$Iopt, maxcop = \frac{\alpha pn\Delta T}{R(\sqrt{1 + ZTm} - 1)} \tag{19}$$

Substituting in equation (12):

$$\mathrm{COP}_{\max} = \frac{\frac{Tc}{\Delta T}\left(\sqrt{1 + ZTm} - \frac{Th}{Tc}\right)}{\sqrt{1 + ZTm} + 1} \tag{20}$$

where $Tm = (Tc + Th)/2$

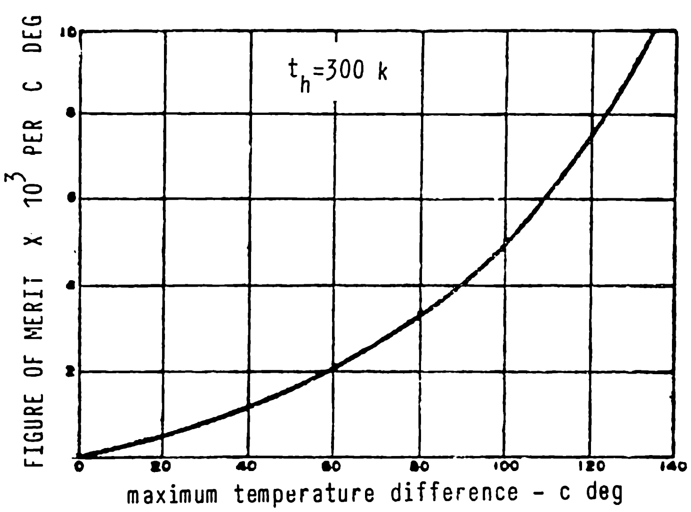

Fig. 4. Maximum Temperature Difference from Room Temperature Produced by a Thermoelectric Couple as a Function of the Figure of Merit

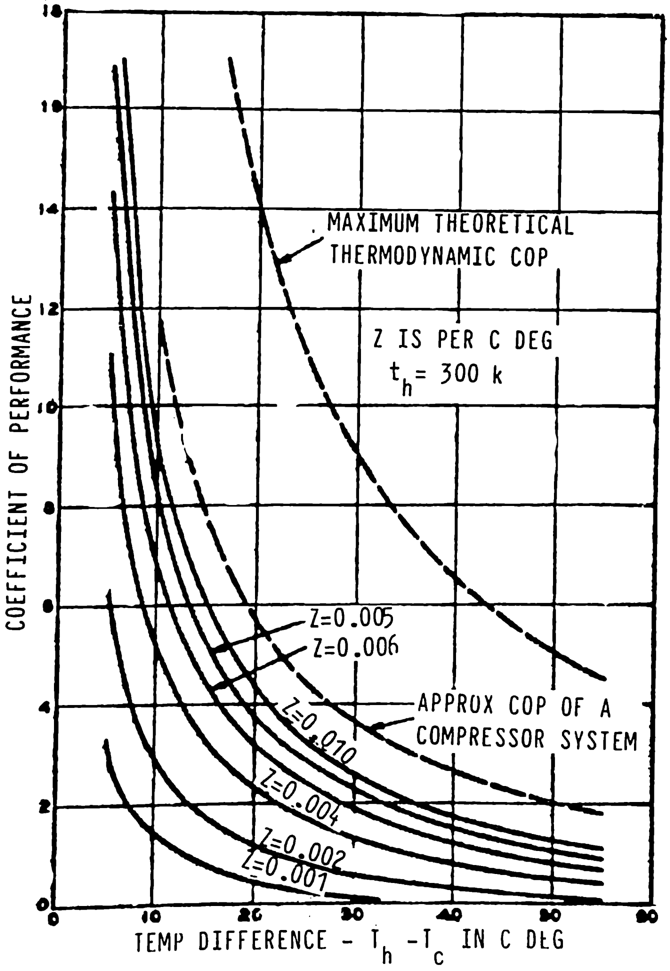

Fig. 5. Maximum Coefficient of Performance of a Thermoelectric Couple as a Function of Temperature Difference and Figure of Merit, Z

The parameter Z is known as the figure of merit and is a function of the thermocouple materials only.

Figures 4 and 5 indicate that the value of the figure of merit is an important parameter in the performance of a thermoelectric cooling couple. Large values of Z are desirable. In order to have a large Z, the couple materials must have a high thermoelectric power α and a small CR (thermal conductance x electrical resistance).

The conductance may be written in terms of the thermal conductivity k, cross-sectional area A, and length L of the elements. Subscripts p and n are for the p-type and n-type materials respectively. Thermal contact resistance is negligible.

$$C = Cp + Cn = kp\frac{Ap}{L} + kn\frac{An}{L} \qquad (21)$$

The electrical resistance R consists principally of the resistances of the elements and the contact resistance between the elements and the connecting strips. Thus

$$R = Rp + Rn = \left(\rho p\frac{L}{Ap} + \frac{2r}{Ap}\right) + \left(\rho n\frac{L}{An} + \frac{2r}{An}\right) \qquad (22)$$

where ρ and r are the electrical resistivity and contact resistance respectively.

To maximize the figure of merit for a given set of materials, we look for the minimum value of CR. Using the same technique as before, we find that

$$\frac{Ap}{An} = \sqrt{\frac{kn\,\rho p\left(1 + \frac{2r}{\rho pL}\right)}{kp\,\rho n\left(1 + \frac{2r}{\rho nL}\right)}} \qquad (23)$$

Equation (23) with equation (17) yields

$$Zmax = \frac{\alpha}{\sqrt{kp\rho p\left(1 + \frac{2r}{pL}\right)} + \sqrt{kn\rho n\left(1 + \frac{2r}{nL}\right)}} \qquad (24)$$

If the couple has equal values of k and ρ, and $\alpha p = -\alpha n$ so that $\alpha = 2\alpha p$ or $2\alpha n$, then equation (24) reduces to:

$$\text{Zmax} = \frac{\alpha^2 \sigma}{k\left(1 + \frac{2r}{\rho L}\right)} \tag{25}$$

$\sigma = \frac{1}{\rho}$ = the electrical conductivity.

The factor $(1 + \frac{2r}{\rho L})$ which represents the presence of contact resistance has an important bearing not only on the actual performance of a couple but also on the economics of thermoelectric cooling today.

Metals are poor thermoelectric materials since they have inherently low thermoelectric power α and high thermal conductivity k although they have high electrical conductivity σ. On the other hand, insulators have high thermoelectric power α and correspondingly low thermal conductivity k but they are very poor electrical conductors. Hence materials somewhere between these two extremes or semi-conductors may give the best results as shown in Figure 6.

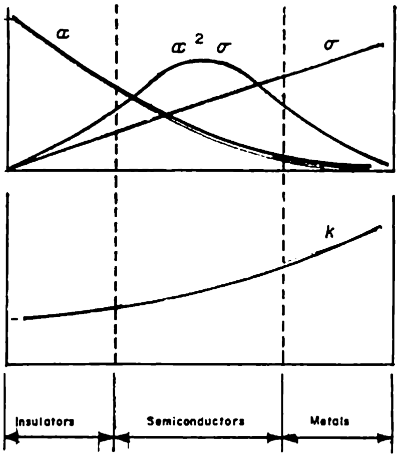

FIGURE 6 Schematic comparative thermoelectric characteristics for insulators, semiconductors, and metals.

At present materials are available with Z ≅ 0.003/degC with typical individual parameters as follows:

α = 0.00021 volt/deg C

ρ = 0.001 ohm-cm

k = 0.015 watt/(cm)(C)

The typical value of electrical contact resistance ranges from 0.00001 to 0.0001 ohm-cm^2.

Applications

The development of thermoelectric refrigeration has been very slow inspite of the rapid development of the semi-conductor in the past 20 years. The high cost of the system and the low system COP seem to be the major reasons for not being able to compete with conventional systems. A breakthrough in the improvement of the figure of merit may usher a new era wherein thermoelectric refrigeration could become a threat to the present day conventional systems.

Some of the advantages include (a) ease of interchanging the cooling and heating functions by simply reversing the polarity of the supplied current, (b) no wear, tear and noise from moving parts, (c) no problem of refrigerant containment, (d) ease of miniaturization for very small capacity applications, (e) generally require smaller space and have lighter components, (f) ease of modulating the capacity by varying the DC voltage applied to the couples either by a variable voltage control or by switching series and parallel circuits or both, (g) reliability and ruggedness, (h) ability to operate under zero gravity or many g's of gravity, and (i) will operate at any orientation or position. The chief drawbacks include low COP and high initial cost.

For some applications however some of the advantages outweigh the disadvantages. Thermoelectric refrigeration systems for submarines and space vehicles are technically and economically feasible. A 9-ton air conditioner was built for a small submarine.

There are also appliance and small commercial refrigeration applications such as a drinking water cooler, a small ice maker for hotel rooms, one (1) cu. ft. portable refrigerators, and a 2-ft^3 unit which could be used as a refrigerator or warming oven to name a few.

Currently, thermoelectric with capacities up to 200 Btu/hr are practical and competitive with compression systems. Figure 7 shows the dramatic improvement in the maximum temperature difference achieved in the recent years.

Design Guide

Materials used for the elements of thermoelectric cooling couples include alloys of bismuth, tellurium, and selenium for n-type elements and alloys of bismuth, tellurium and antimony for p-type elements.

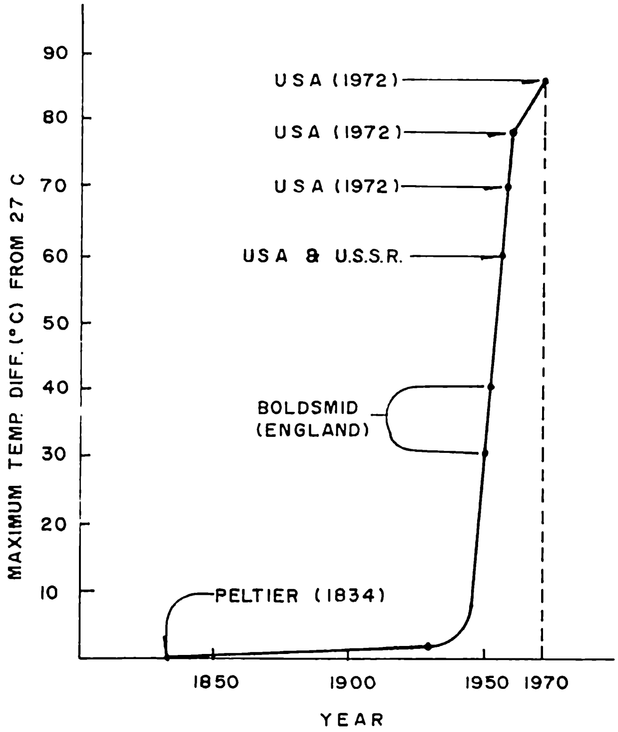

FIG. 7 MAXIMUM TEMPERATURE DIFFERENCE ACHIEVED WITH A THEMOELECTRIC COUPLE OVER THE YEARS

Figure 8 shows a schematic cross section of a thermoelectric module showing the thermocouple elements, finned heat exchangers, vapor barrier, thermal insulation and electrical insulation. Moisture that condenses on the cold side must be kept from reaching the thermoelectric junction to prevent electrochemical action from causing failure at the junction.

Since for a given current (see Figure 9) an increase in temperature difference across the couple has an appreciable effect on the cooling capacity Qi, it is important to minimize the temperature difference between the hot junction and the coolant and between the cold junction and the fluid being cooled.

Several manufacturers have come up with different standard modules in different current rating and different number of couples. One approach is to simply select from available modules to fit a given requirement. Figures 10 through 14 show several typical thermoelectric modules and some typical technical data for some commercially available models of modules.

A sample calculation for a cascaded air-cooled thermoelectric refrigerator-freezer is found in the Appendix.

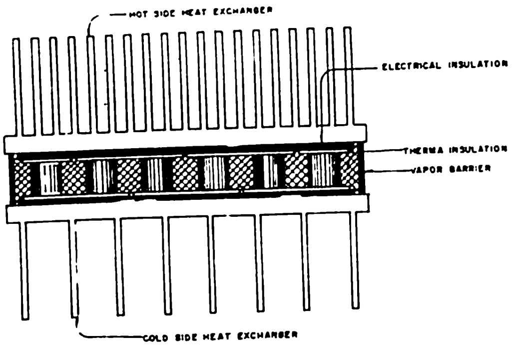

FIG. 8 CROSS SECTION OF THERMOELECTRIC MODULE AND TRANSFER SURFACES

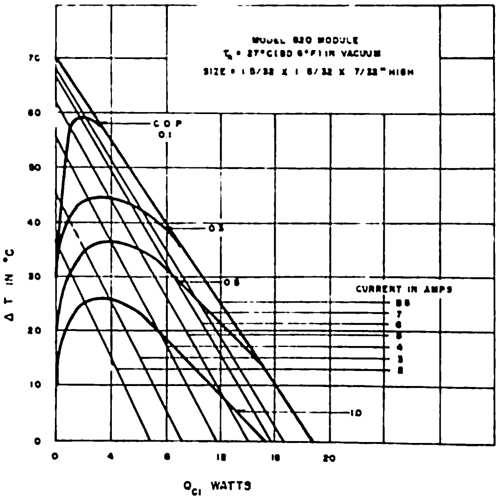

FIG. 11 MODULE ΔT VS MODULE HEAT PUMPING CAPACITY FOR VARIOUS COP AND CURRENT VALUES

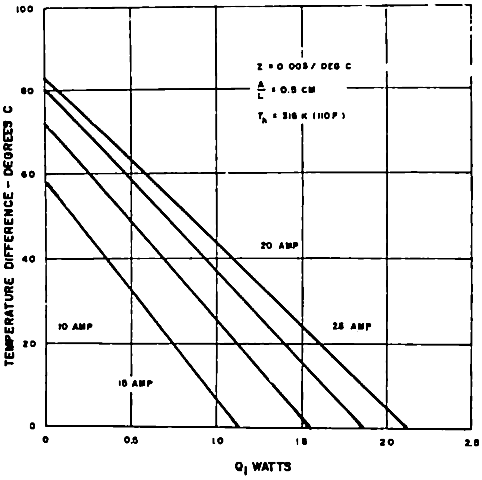

FIG. 9 HEAT PUMPING CAPACITY OF A THERMOELECTRIC COUPLE AS A FUNCTION OF A TEMPERATURE DIFFERENCE AND CURRENT.

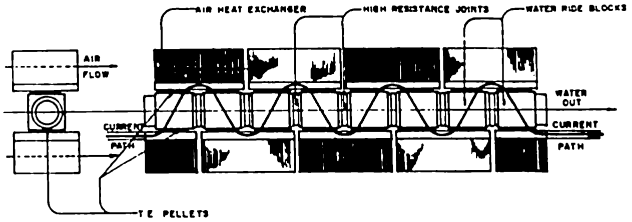

FIG. 12 GENERAL ARRANGEMENT OF COMPONENTS FOR WATER-AIR THERMOELECTRIC MODULE

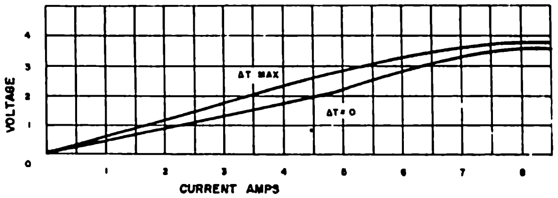

FIG. 13 MODULE VOLTAGE

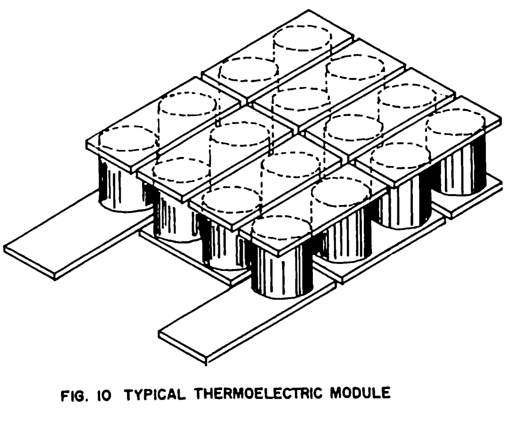

FIG. 10 TYPICAL THERMOELECTRIC MODULE

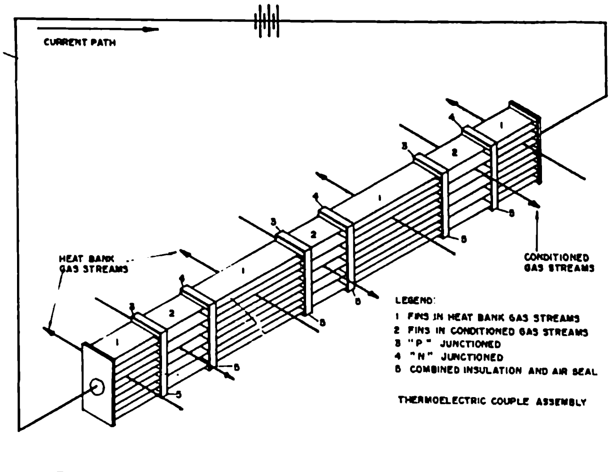

FIG 14 MODIFIED COUPLE FOR GAS-TO-GAS HEAT TRANSFER

APPENDIX

Calculations for an Air-cooled Thermoelectric Refrigerator-Freezer

A refrigerator with a fractional cascade of two thermoelectric cooling stages is to be designed: the lower stage provides cooling for a freezer compartment; the upper stage provides cooling for a food compartment and for the lower stage hot junction.

Design Requirements:

A two-temperature 2 cu. ft. refrigerator capable of maintaining a freezer temperature of −10C and a refrigerator temperature of 10C at an ambient temperature of +35C(95F).

Design Capacity

20 watts (68 Btu/hr) for food compartment, 10 watts (34 Btu/hr) for freezer compartment.

Maximum Design Conditions:

1. Allow 5C temperature gradient between the freezer compartment and the freezer cold junction. Also between the refrigerator compartment and the refrigerator cold junction.

2. Allow 3C temperature difference between the low-stage hot junction and the refrigerator cold junction.

3. Therefore,

a) for the 1st stage: $t_{c1} = -15C$, $t_{h1} = +8C$, $\Delta t_1 = 23C$

b) for the 2nd stage: $t_{c2} = 5C$, $t_{h2} = 45C$, $\Delta t = 40C$

Thermocouples:

Each element has a length of 6.35 mm, a diameter of 7 mm,

$|\alpha_p| = |\alpha_n| = 2.0 \times 10^{-4}$ volt/C, $\rho = 8.3 \times 10^{-4}$ ohm-cm, $k = 1.6 \times 10^{-2}$ watt/cm C.

Mode of Operation:

Maximum COP

Determine:

(a) Total heat rejection at final heat dissipation surface

(b) Total input DC power requirement

(c) Overall COP

(d) Number of couples

(e) Current and voltage requirements

Solution

For each couple,

$$L = 6.35 \text{ mm}, \frac{A}{L} = \frac{\frac{\pi}{4}(7)^2}{6.35} = 6.06 \text{ mm} = 0.606 \text{ cm}$$

$$R = 2\frac{L}{A}\rho = 2\left(\frac{1}{0.606}\right)(8.3 \times 10^{-4}) = 2.74 \times 10^{-3} \text{ ohm}$$

$$C = 2\frac{A}{L}k = 2(0.606)(1.6 \times 10^{-2}) = 1.94 \times 10^{-2} \text{ watt/C}$$

$$Z = \frac{\alpha^2}{CR} = \left(\frac{T_c}{Th - Tc}\right)\frac{\sqrt{1 + ZT_m - T_h/T_c}}{\sqrt{1 + ZT_m + 1}},$$

where T_h = hot junction temp.

T_c = cold junction temp.

$T_m = \frac{1}{2}(T_h + T_c)$

First Stage: $\Delta T_1 = 23C, T_c = -15 + 273 = 258K, T_h = 8 + 273 = 281K,$

$$T_m = \frac{258 + 281}{2} = 269.5 \text{ K}$$

$$(\text{COP})_{\max_1} = \left(\frac{258}{23}\right)\frac{\sqrt{1 + 0.003(269.5)} - (281/258)}{\sqrt{1 + 0.0003(269.5)} + 1} = 1.22$$

Second Stage: $\Delta T_2 = 40C, T_c = 5 + 273 \text{ K}, T_h = 45 + 273 = 318 \text{ K}$

$$T_m = 298 \text{ K}$$

$$(\mathrm{COP})_{\mathrm{max}_2} = 0.682$$

Heat and power requirements:

First Stage: Input power $W_1 = \dfrac{(Q_i)_1}{(\mathrm{COP})_1} = \dfrac{10}{1.22} = 8.20$ watts

Heat dissipation at hot junction

$$(Q_0)_i = (Q_i)_1 + W_1 = 10 + 8.20 = 18.2 \text{ watts}$$

Second Stage: Total cooling Load $(Q_i)_2 = 20 + (Q_0)_1 = 20 + 18.2$

$= 38.2$ watts

Input power $W_2 = \dfrac{38.2}{0.682} = 56.0$ watts

(a) Heat dissipation $(Q_0)_2 = 56.0 + 38.2 = 94.2$ watts

(b) Total power input $W = W_1 + W_2 = 8.2 + 56.0 = 64.2$ watts

(c) Overall COP $= \dfrac{(Q_i)_1 + (Q_i)_2}{W_1 + W_2} = \dfrac{10 + 20}{64.2} = 0.467$

Adding 10% for losses in power supply, COP $= \dfrac{30}{70.6} = 0.425$

Note: For a single-stage refrigerator with $\Delta T = 45 - (-15) = 60\mathrm{C}$

$$(\mathrm{COP})_{\mathrm{max}} = \left(\frac{258}{60}\right)\frac{\sqrt{1 + 0.003(228)} - (318/258)}{\sqrt{1 + 0.003(288)} + 1} = 0.241$$

The COP of 0.425 is 70% better than the 0.25 COP of a similar electrically-operated absorption type refrigerator (which has a less effective freezer) and approximately half as good as the smallest hermetic compressor units (which may be noisy, bulky, and have service problems).

(d) For maximum COP

$$I_{\mathrm{opt}} = \frac{(\alpha_p - \alpha_n)(T_h - T_c)}{R(\sqrt{1 + ZT_m} - 1}$$

First Stage $T_m = 269.5$ K

$$I_{\mathrm{opt}_1} = \frac{(4 \times 10^{-4})(318 - 278)}{(2.74 \times 10^{-3})(\sqrt{1 + 0.003(269.5)} - 1)} = 9.74 \text{ amp}$$

Second Stage $T_m = 298$ K

$$I_{opt_2} = \frac{(4 \times 10^{-4})(318 - 278)}{(2.74 \times 10^{-3})(\sqrt{1 + 0.003(298)} - 1)} = 15.52 \text{ amp}$$

Cooling Capacity per couple:

$$q_i = (\alpha_p - \alpha_n)\, T_c I - C(T_h - T_c) - \frac{1}{2} I^2 R$$

First Stage: $(q_i)_1 = (4 \times 10^{-4})(258)(9.74) - (1.94 \times 10^{-2})(23)$

$$- \frac{1}{2}(9.74)^2 (2.74 \times 10^{-3})$$

$= 0.429$ watt/couple

Number of couples:

$$N_1 = \frac{15 \text{ watts}}{0.428 \text{ watt/couple}} = \underline{35}$$

Second Stage:

$$(q_i)_2 = (4 \times 10^{-4})(278)(15.52) - (1.94 \times 10^{-2})(40) - \frac{1}{2}$$

$$(15.52)^2 (2.74 \times 10^{-3})$$

$$= 1.728 - 0.776 - 0.330$$

$= 0.620$ watt/couple

Number of couples:

$$N = \frac{38.2}{0.620} = \underline{62}$$

(e) Total current $I = I_1 + I_2 = 9.74 + 15.52 = \underline{25.26}$ amp

Total power $W = W_1 + W_2 = 8.2 + 56.0 = 64.2$ watts

Voltage drops: First Stage $\Delta E_1 = \frac{W_1}{I_1} = \frac{8.2}{9.74} = 0.842$ volts

Second Stage $\Delta E_2 = -$

Second Stage $\Delta E_2 = \frac{W_1}{I_2} = \frac{56.0}{15.52} = 3.61$ volts

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