Lord Kelvin, by performing a thermodynamic analysis of such a thermoelectric circuit, showed that a relationship exists between $\alpha$ and $\pi$, namely:

$$\pi = \alpha T \tag{3}$$

*where*

$T$ = the absolute temperature, Kelvin.

Hence, the heat absorbed or evolved per unit time at the junction between two dissimilar materials is given by:

$$Q = \alpha_{AB} I T \tag{4}$$

Although thermodynamicists do not accept Kelvin's derivation of his well known relations because he considered the effects to be reversible, a more rigorous treatment, by the application of irreversible thermodynamics, leads to the same results.

The relatively hot and cold surfaces shown in Fig. 2 are the result of the basic heat transport phenomenon called the Peltier effect, and are not necessary to make it occur.

Investigations in solid state physics have shown that thermoelectric refrigeration is a means of heat pumping which utilizes the energy level change in electrons for transporting thermal energy. Electrons flowing across a junction of two dissimilar thermoelectric materials, i.e., materials with different available electron energy levels, must undergo an energy change which results in either the evolution or absorption of heat. The direction of current flow determines which will occur. The bibliography lists several sources of detailed information on solid state theory.

There are two additional effects always present in an ideal thermoelectric circuit which limit its performance. These are the Joule heating effect, which occurs throughout the two materials, and the conduction of heat between the two junctions, which is an inevitable consequence of their being at different temperatures.

## PERFORMANCE OF THERMOELECTRIC COUPLES

A complete circuit consisting of two dissimilar thermoelectric materials is referred to as a couple. A typical couple is shown in Fig. 3. The two thermoelectric materials are represented by $n$ and $p$. The $n$-type has a negative Seebeck coefficient and an excess of electrons. The $p$-type has a positive Seebeck coefficient and a deficiency of electrons. The current is shown in the conventional direction; electrons actually flow in the opposite direction. While there are a total of four

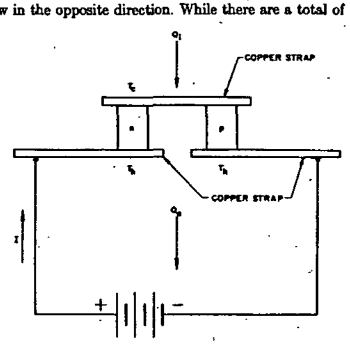


Fig. 3 . . . . Peltier Thermoelectric Couple

connections between the thermoelectric materials and the copper straps, there are only two thermoelectric junctions, the upper or cold one, at which heat is absorbed, and the lower or hot one, at which heat is evolved. If the direction of current were reversed, the upper junction would evolve heat and the lower would absorb it.

The temperature gradient between the hot and cold junctions is not linear, because of the production of Joule heat within each leg. The conducted heat arriving at the cold junction is given by:

$$C\Delta T + \tfrac{1}{2}I^2R$$

*where*

$C$ = thermal conductance of couple legs, watts per Centigrade degree.

Thermal conductance, as used in this chapter, is the rate of heat conduction per unit temperature difference between opposite parallel faces of a rectangular or cylindrical section of material. It is not to be confused with the term thermal conductance, used in other chapters, which refers to rate of heat conduction *per unit area*. Such would not be a convenient concept to employ in thermoelectric device theory.

$R$ = electrical resistance of couple legs, ohms,

while the heat leaving the hot junction by conduction is:

$$C\Delta T - \tfrac{1}{2}I^2R$$

This can be shown by deducing the heat flow in a bar of material in which heat is produced by virtue of an electric current passing through it while its two ends are simultaneously maintained at different temperatures.

By considering the steady state condition at the cold junction and the total input power, one may deduce the characteristics of such a couple. The following assumptions are made:

(a) The parameters $\alpha$, $\rho$ (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) The electrical resistance of the copper connecting strips and of the contacts between the copper and the semiconductor is negligible.

When a steady state is established at the cold junction, the Peltier cooling equals the heat conducted down the couple legs, plus the ambient heat absorbed (useful heat pumped):

$$\alpha_{pn} T_c I = C\Delta T + \tfrac{1}{2}I^2R + Q_i$$

or

$$Q_i = \alpha T_c I - \tfrac{1}{2}I^2R - C\Delta T \tag{5}$$

*where*

$Q_i$ = rate of heat absorbed at cold junction, watts.

$\alpha = \alpha_{pn} = \alpha_p - \alpha_n$ = the difference between the absolute Seebeck coefficients of the $p$ and $n$ materials.

$\Delta T = (T_h - T_c)$ = operating temperature difference, Centigrade degrees.

$T_h$ = hot junction temperature, Kelvin degrees.

$T_c$ = cold junction temperature, Kelvin degrees.

$R = R_n + R_p$, electrical resistances of couple legs, ohms.

$C = C_n + C_p$, thermal conductances of the couple legs, watts per Centigrade degree.

The resistances of the couple legs are:

$$R_n = \rho_n \frac{L_n}{A_n} \qquad R_p = \rho_p \frac{L_p}{A_p}$$

*where*

$\rho_n$, $\rho_p$ = electrical resistivities of the couple legs, ohm centimeters.



$L_n$, $L_p$ = length of the couple legs, centimeters.

$A_n$, $A_p$ = cross sectional areas of the couple legs, square centimeters.

The thermal conductances are:

$$C_n = K_n \frac{A_n}{L_n} \qquad C_p = K_p \frac{A_p}{L_p}$$

*where*

$K_n$, $K_p$ = thermal conductivities of couple legs, watts per (square centimeter) (Centigrade degree per centimeter).

The power required to obtain the rate of cooling shown in Equation 5 is:

$$W = IV = I(IR + \alpha\Delta T) \tag{6}$$

*where*

$W$ = power input, watts.

$V$ = applied voltage, volts.

The applied voltage is the sum of two terms, the voltage drop which always occurs in an electrical conductor, plus that required to overcome the Seebeck voltage.

The coefficient of performance for a thermoelectric refrigerating system is the same as for any other refrigerating system, or the rate of cooling divided by the power input:

$$\phi = \frac{Q_i}{W} = \frac{\alpha T_c I - \tfrac{1}{2}I^2R - C\Delta T}{I^2R + \alpha\Delta T I} \tag{7}$$

*where*

$\phi$ = coefficient of performance, dimensionless.

While the proof will not be given, it can be shown that, in order to maximize $Q_i$, it is necessary to have a specific geometry for the couple legs. This is:

$$\frac{A_p/L_p}{A_n/L_n} = \sqrt{\frac{K_n\rho_p}{K_p\rho_n}} \tag{8}$$

Unless otherwise stated, this optimum geometry is used in developing the remainder of the equations in this section.

The maximum coefficient of performance (CP) is obtained by using Equation 7 (with the optimum couple geometry from Equation 8 included) and differentiating the CP with respect to $I$. Equating this to zero and solving for $I$ gives:

$$I\phi_{(max)} = \frac{\alpha\Delta T}{(M-1)R} \tag{9}$$

and substituting Equation 9 into Equation 7 gives:

$$\phi_{(max)} = \frac{T_c}{T_h - T_c} \times \frac{M - (T_h/T_c)}{M+1} \tag{10}$$

*where*

$$M = \sqrt{1 + \frac{\alpha^2}{(\sqrt{K_p\rho_p} + \sqrt{K_n\rho_n})^2}\left[\frac{T_h + T_c}{2}\right]}$$

Thus, it is seen that $\phi_{(max)}$ is dependent only on the operating temperatures, the Seebeck coefficient, and the electrical and thermal conductivities of the two materials comprising the couple. The value of $T_c/\Delta T$ represents the coefficient of performance of a reversible process. The expression containing these material parameters is referred to as the *Figure of Merit*[1,2] of the couple and is denoted by $Z$ (in reciprocal Kelvin degrees). Thus:

$$Z = \frac{\alpha^2}{(\sqrt{K_p\rho_p} + \sqrt{K_n\rho_n})^2} \tag{11}$$

If the corresponding thermoelectric parameters are equal in each material, then $Z$ reduces to:

$$\frac{\alpha_p^2}{K_p\rho_p} \text{ or } \frac{\alpha_n^2}{K_n\rho_n}$$

and these two expressions are equal to each other The $Z$ value is the most important overall parameter associated with a thermoelectric material. The higher its value, the better the performance of a thermoelectric couple. From the expression for $Z$ it is seen that a high Seebeck coefficient, low electrical resistivity, and low thermal conductivity are essential.

Substituting the value of $I$ from Equation 9 in Equation 5 gives the heat pumping rate at conditions of maximum CP:

$$Q_i\phi_{(max)} = \frac{2C\Delta T M[M - (T_h/T_c)]}{(M-1)[1 + (T_h/T_c)]}$$

The temperature difference obtained with a thermoelectric couple is determined by the thermal load and is maximum under no load conditions ($Q_i = 0$), which gives:

$$\Delta T_{(max)} = \frac{1}{C}(\alpha I T_c - \tfrac{1}{2}I^2R) \tag{12}$$

By differentiating Equation 12 with respect to current, the optimun current is found to be:

$$I = \frac{\alpha T_c}{R} \tag{13}$$

and

$$\Delta T_{(max)} = \tfrac{1}{2}ZT_c^2 \tag{14}$$

Thus, it is seen that, like the maximum coefficient of performance, the maximum temperature difference is dependent only on temperature and the figure of merit.

The maximum heat pumped by a couple for a given temperature difference is obtained by using Equation 5 and differentiating with respect to $I$. The current for this condition is found to be:

$$I_{Q_i(max)} = \frac{\alpha T_c}{R}$$

which is the same as for the maximum $\Delta T$ (see Equation 13).

Substituting this value of current into Equation 5:

$$Q_{i(max)} = \tfrac{1}{2}\frac{\alpha^2 T_c^2}{R} - C\Delta T$$

or

$$Q_{i(max)} = C(\Delta T_{(max)} - \Delta T) \tag{15}$$

The coefficient of performance at maximum heat pumping is found by substituting the value for $I$ from Equation 13 in Equation 7

$$\phi_{Q_i(max)} = \frac{\Delta T_{(max)} - \Delta T}{ZT_hT_c} \tag{16}$$

This approaches the limiting value of 0.5 as $\Delta T$ approaches zero. It will be seen from Equation 15 that the heat absorbed per couple for a given $Z$ value is proportional to $C$ and is therefore a function of the ratio $A/L$ for each leg. As this increases, the heat pumping capacity per couple increases, but so does the optimum current since it is inversely proportional to $R$.

The important formulas for computing couple performance are listed for easy reference:

(a) $\Delta T_{max} = \tfrac{1}{2}ZT_c^2$

(b) $Q_{imax} = C(\Delta T_{max} - \Delta T)$