Chapter 5  Thomson Effect, Exact Solution, and Compatibility Factor

Contents

Chapter 5  Thomson Effect, Exact Solution, and Compatibility Factor........................................5-1
  Contents ......................................................................................................................................5-1
  5.1  Thermodynamics of Thomson Effect ....................................................................................5-2
  5.2  Exact Solutions ....................................................................................................................5-10
      5.2.1  Equations for the Exact solutions and the Ideal Equation ............................................5-10
      5.2.2  Thermoelectric Generator .............................................................................................5-13
      5.2.3  Thermoelectric Coolers ...............................................................................................5-15
  5.3  Compatibility Factor .............................................................................................................5-18
  5.4  Thomson Effects ..................................................................................................................5-29
      5.4.1  Formulation of Basic Equations .....................................................................................5-30
      5.4.2  Numeric Solutions of Thomson Effect ...........................................................................5-36
      5.4.3  Comparison between Thomson Effect and Ideal Equation ........................................5-40
  Problems ......................................................................................................................................5-44
  Projects .......................................................................................................................................5-44
  References ....................................................................................................................................5-45
The formulation of the classical basic equations for a thermoelectric cooler from the Thomson relations to the non-linear differential equation with Onsager’s reciprocal relations was performed to study the Thomson effect in conjunction with the ideal equation. The ideal equation is obtained when the Thomson coefficient is assumed to be zero. The exact solutions derived for a commercial thermoelectric cooler module provide the temperature distributions including the Thomson effect. The positive Thomson coefficient led to a slight improvement on the performance of the thermoelectric device while the negative Thomson coefficient led to a slight decline in the performance. The comparison between the exact solutions and the ideal equation on the cooling power and the coefficient of performance over a wide range of temperature differences showed close agreement. The Thomson effect is small for typical commercial thermoelectric coolers and the ideal equation effectively predicts the performance.

5.1 Thermodynamics of Thomson Effect

The thermoelectric effect consists of three effects: the Seebeck effect, the Peltier effect, and the Thomson effect.

**Seebeck Effect**

The *Seebeck effect* is the conversion of a temperature difference into an electric current. As shown in Figure 5.1, wire A is joined at both ends to wire B and a voltmeter is inserted in wire B. Suppose that a temperature difference is imposed between two junctions, it will generally found that a potential difference \( \Delta \phi \) or voltage \( V \) will appear on the voltmeter. The potential difference is proportional to the temperature difference. The potential difference \( V \) is

\[
V = \alpha_{AB} \Delta T
\]
where $\Delta T = T_H - T_L$ and $\alpha$ is called the Seebeck coefficient (also called thermopower) which is usually measured in $\mu V/K$. The sign of $\alpha$ is positive if the electromotive force, $emf$, tends to drive an electric current through wire A from the hot junction to the cold junction as shown in Figure 5.1. The relative Seebeck coefficient is also expressed in terms of the absolute Seebeck coefficients of wires A and B as

$$\alpha_{AB} = \alpha_A - \alpha_B$$

(5.2)

Figure 5.1 Schematic basic thermocouple.

In practice one rarely measures the absolute Seebeck coefficient because the voltage meter always reads the relative Seebeck coefficient between wires A and B. The absolute Seebeck coefficient can be calculated from the Thomson coefficient.

**Peltier Effect**

When current flows across a junction between two different wires, it is found that heat must be continuously added or subtracted at the junction in order to keep its temperature constant, which is shown in Figure 5.2. The heat is proportional to the current flow and changes sign when the current is reversed. Thus, the Peltier heat absorbed or liberated is

$$\dot{Q}_{\text{Peltier}} = \pi_{AB} I$$

(5.3)
where $\pi_{AB}$ is the Peltier coefficient and the sign of $\pi_{AB}$ is positive if the junction at which the current enters wire $A$ is heated and the junction at which the current leaves wire $A$ is cooled. The Peltier heating or cooling is reversible between heat and electricity. This means that heating (or cooling) will produce electricity and electricity will produce heating (or cooling) without a loss of energy.

![Figure 5.2 Schematic for the Peltier effect and the Thomson effect.](image)

**Thomson Effect**

When current flows in wire $A$ as shown in Figure 5.2, heat is absorbed due to the negative temperature gradient and liberated in wire $B$ due to the positive temperature gradient, which relies on experimental observations [1, 2], depending on the materials. It is interesting to note that the wire temperature in wire $B$ actually drops because the heat is liberated while the wire temperature in wire $A$ rises because the heat is absorbed, which is clearly seen in the work of Amagai and Fujiki (2014) [1, 2]. The Thomson heat is proportional to both the electric current and the temperature gradient. Thus, the Thomson heat absorbed or liberated across a wire is

$$\dot{Q}_{\text{Thomson}} = -\tau I \nabla T \quad (5.4)$$

where $\tau$ is the Thomson coefficient. The Thomson coefficient is unique among the three thermoelectric coefficients because it is the only thermoelectric coefficient directly measurable.
for individual materials. There is other form of heat, called Joule heating, which is irreversible and is always generated as current flows in a wire. The Thomson heat is reversible between heat and electricity. This heat is not the same as Joule heating, or $I^2R$.

**Thomson (or Kelvin) Relationships**

The interrelationships between the three thermoelectric effects are important for understanding the basic phenomena. In 1854, Thomson [3] studied the relationships thermodynamically and provided two relationships by applying the *first and second laws of thermodynamics* with an assumption that the reversible and irreversible processes in thermoelectricity are separable. The necessity for the assumption remained an objection to the theory until the advent of the new thermodynamics. The relationships were later completely confirmed by experiment being essentially a consequence of Onsager’s Principle (1931) [4]. It is not surprising that, since the thermal energy and electrostatic energy in quantum mechanics are often reversible, those in thermoelectrics are reversible.

For a small temperature difference, the Seebeck coefficient is expressed in terms of the potential difference per unit temperature, as shown in Equation (5.1).

\[
\frac{\Delta \phi}{\Delta T} = \frac{d\phi}{dT} = \alpha_{AB} \tag{5.5}
\]

where $\phi$ is the electrostatic potential and $\alpha$ is the Seebeck coefficient that is a driving force and is referred to as thermopower.

Consider two dissimilar wires A and B constituting a closed circuit (Figure 5.3), in which the colder junction is at a temperature $T$ and the hotter junction is at $T + \Delta T$ and both are maintained by large heat reservoirs. Two additional reservoirs are positioned at the midpoints of wires A and B. Each of these reservoirs is maintained at a temperature that is the average of those at the hotter and colder junctions.
It is assumed that the thermoelectric properties such as the Seebeck, Peltier and Thomson coefficients remain constant with the passage of a small current. In order to study the relationships between the thermoelectric effects, a sufficiently small temperature difference is to be applied between the two junctions as shown in Figure 5.3. It is then expected that a small counter clockwise current flows (this is the way that the dissimilar wires A and B are arranged).

We learned earlier that thermal energy is converted to electrical energy and that the thermal energy constitutes the Peltier heat and the Thomson heat, both of which are reversible. The difficulty is that the circuit inevitably involves irreversibility. The current flow and the temperature difference are always accompanied by Joule heating and thermal conduction, respectively, both of which are irreversible and make no contribution to the thermoelectric effects. Thomson assumed that the reversible and irreversible processes are separable. So the reversible electrical and thermal energies can be equated using the first law of thermodynamics.

\[
I \Delta \phi = I \pi_{AB}(T + \Delta T) - I \pi_{AB}(T) + \tau_B I \Delta T - \tau_A I \Delta T
\]

(5.6)
For a small potential difference due to the small temperature difference, the potential difference is expressed mathematically as

\[ \Delta \phi = \frac{d\phi}{dT} \Delta T \]  

(5.7)

Using this and dividing Equation (5.6) by the current \( I \) gives

\[ \frac{d\phi}{dT} \Delta T = \pi_{AB}(T + \Delta T) - \pi_{AB}(T) + (\tau_B - \tau_A)\Delta T \]  

(5.8)

Dividing this by \( \Delta T \) gives

\[ \frac{d\phi}{dT} = \frac{\pi_{AB}(T + \Delta T) - \pi_{AB}(T)}{\Delta T} + (\tau_B - \tau_A) \]  

(5.9)

Since \( \Delta T \) is small, we conclude

\[ \frac{d\phi}{dT} = \frac{d\pi_{AB}}{dT} + (\tau_B - \tau_A) \]  

(5.10)

which is nothing more than the Seebeck coefficient as defined in Equation (5.5). This is the fundamental thermodynamic theorem for a closed thermoelectric circuit; it shows the energy relationship between the electrical Seebeck effect and the thermal Peltier and Thomson effects. The potential difference, or in other words the electromotive force (emf), results from the Peltier heat and Thomson heat or vice versa. More importantly the Seebeck effect is directly caused by both to the Peltier and Thomson effects.
The assumption of separable reversibility imply that the net change of entropy of the surroundings (reservoirs) of the closed circuit is equal to zero. The results are in excellent agreement with experimental findings [6]. The net change of entropy of all reservoirs is zero because the thermoelectric effects are reversible, so we have

\[ \Delta S = -\frac{Q_{\text{at junction}}}{T+\Delta T} + \frac{Q_{\text{at junction}}}{T} - \frac{Q_{\text{along wire B}}}{T+\Delta T/2} + \frac{Q_{\text{along wire A}}}{T+\Delta T/2} = 0 \] (5.11)

Using Equations (5.3) and (5.4)

\[ -\frac{I\pi_{\text{AB}}(T+\Delta T)}{T+\Delta T} + \frac{I\pi_{\text{AB}}(T)}{T} - \frac{\tau_B I\Delta T}{T+\Delta T/2} + \frac{\tau_A I\Delta T}{T+\Delta T/2} = 0 \] (5.12)

Dividing this by \(-I\Delta T\) yields

\[ \frac{\pi_{\text{AB}}(T+\Delta T)}{T+\Delta T} - \frac{\pi_{\text{AB}}(T)}{T} + \frac{\tau_B}{T+\Delta T/2} - \frac{\tau_A}{T+\Delta T/2} = 0 \] (5.13)

Since \(\Delta T\) is small and \(\Delta T/2 \ll T\), we have

\[ \frac{d}{dT} \left( \frac{\pi_{\text{AB}}}{T} \right) + \frac{\tau_B - \tau_A}{T} = 0 \] (5.14)

By taking the derivative in the first term, we have
\[ T \frac{d\pi_{AB}}{dT} - \frac{\pi_{AB}}{T^2} + \frac{T_B - T_A}{T} = 0 \]  

(5.15)

which reduces to

\[ \frac{\pi_{AB}}{T} = \frac{d\pi_{AB}}{dT} + \frac{T_B - T_A}{T} \]  

(5.16)

Combining Equations (5.10) and (5.14) yields

\[ \frac{d\phi}{dT} = \frac{\pi_{AB}}{T} \]  

(5.17)

Using Equation (5.5), we have a very important relationship as

\[ \pi_{AB} = \alpha_{AB} T \]  

(5.18)

Combining Equations (5.14) and (5.17) gives

\[ T_A - T_B = T \frac{d\alpha_{AB}}{dT} \]  

(5.19)

Equations (5.18) and (5.19) are called the Thomson (Kelvin) relationships. By combining Equations (5.3) and (5.18), the thermal energy caused solely by the Seebeck effect is derived,

\[ Q_{\text{Peltier}} = \alpha_{AB} T I \]  

(5.20)
which is one of most important thermoelectric equations. By taking the integral of Equation (5.19) after dividing it by $T$, the Seebeck coefficient has an expression in terms of the Thomson coefficients. Since the Thomson coefficients are measurable, the Seebeck coefficient can be calculated from them.

$$\alpha_{AB} = \int_{0}^{T} \frac{T_{A}}{T} dT - \int_{0}^{T} \frac{T_{B}}{T} dT$$ (5.21)

### 5.2 Exact Solutions

#### 5.2.1 Equations for the Exact solutions and the Ideal Equation

The ideal equation has been widely used in science and engineering. It was previously shown that the Thomson effect is small for commercial thermoelectric cooler modules. However, here we develop an exact solution considering temperature-dependent material properties including the Thomson effect and determine the error of the ideal equation. Assume that the electric current and heat flux can be considered one-dimensional conserved quantities in a thermoelectric element as shown in Figure 5.4. The original work on this topic was discussed by Mahan (1991)[7] and later McEnaney et al. (2011) [8].
From Equation (5.91), we have

\[
\frac{dT}{dx} = \frac{\alpha Tj - q}{k} \tag{5.22}
\]

From Equation (5.82), (5.83) and (5.91), we have

\[
\frac{dq}{dx} = \rho j^2 + j \alpha \frac{\alpha Tj - q}{k} \tag{5.23}
\]

These are called the exact solutions. These equations can be solved simultaneously numerically for a thermoelectric element in Figure 5.4 to find the temperature distribution and the heat flux profile within the element. This basic framework for determining the performance of a thermoelectric element can be incorporated into finding the efficiency of a thermoelectric generator with multiple thermoelectric elements, either a single stage, segmented, or cascaded architecture [7, 8]. Note that these equations can handle the temperature-dependent material properties. These solutions are the exact solution. For the solution, two boundary conditions at \( x = 0 \) and \( x = L \) are needed and either the current can be provided from Equation (5.86) for a
thermoelectric generator or a constant current is given for a thermoelectric cooler. One of the difficulties in computations for the exact solution is that Equation (5.22) and (5.23) can be solved algebraically or numerically. Sometimes non-dimensionality is helpful for a mathematical program.

Now, we want to examine the ideal equation solution by comparing it with the exact solution to determine the uncertainty of the ideal equation. We can solve numerically for the temperature profile and the heat flux for both the ideal equation and the exact solution with the real thermoelectric material of skutterudite. The ideal equation for the temperature distribution and the heat flux profile can be obtained from Equation (5.93), which is rewritten as

$$\nabla \cdot (k \nabla T) + j^2 \rho - T \frac{d\alpha}{dT} \cdot \nabla T = 0$$

(5.24)

For the ideal equation, it is assumed that \( \frac{d\alpha}{dT} = 0 \) which eliminates the Thomson effect. Solving Equation (5.24) for \( \frac{dT}{dx} \) gives

$$\frac{dT}{dx} = \frac{\rho j^2 L}{k} \left( 1 - \frac{x}{L} \right) - \frac{T_h - T_c}{L}$$

(5.25)

The temperature distribution is obtained by integrating the above equation, which is

$$T(x) = \frac{\rho j^2 L^2}{2k} \left[ \frac{x}{L} - \left( \frac{x}{L} \right)^2 \right] + T_h - (T_h - T_c) \frac{x}{L}$$

(5.26)

From Equation (5.91) with (5.25), the heat flux as a function of the element distance \( x \) is

$$q(x) = \rho j^2 L \left( \frac{x}{L} - 1 \right) + (T_h - T_c) \frac{k}{L} + \alpha T j$$

(5.27)
These two equations for the ideal equation can be solved with the material properties at a mid-temperature between $T_h$ and $T_c$.

### 5.2.2 Thermoelectric Generator

In this section, the subscript 1 and 2 denote high and low quantities, respectively, such as $T_1 = T_h$ and $T_2 = T_c$ in Figure 5.4. The material properties for typical skutterudites [9] used in this calculation are shown in Figure 5.5.

![Figure 5.5](image)

**Figure 5.5** The curve fitting from experimental data for skutterudite by Shi et al. (2011)[9]. (a) Seebeck coefficient, curve fit: $\alpha(T) = (60.703 + 0.2482T - 0.0001T^2) \times 10^{-6} V/K$, (b)
thermal conductivity, \( k(T) = (2.388 + 0.0025T - 6 \times 10^{-6}T^2 + 4 \times 10^{-9}T^3) \, W/mK \), (c)
electrical conductivity, \( \rho(T) = (1.1527 + 0.0111T + 4 \times 10^{-6}T^2) \times 10^{-6} \Omega m \), and (d)
dimensionless figure of merit.

Computations for the exact solution and the ideal equation for a thermoelectric generator with
the temperature-dependent material properties for typical skutterudites were conducted. The high
and low junction temperatures are maintained as \( T_1 = 800 \, K \) and \( T_2 = 400 \, K \), respectively. The
thermoelectric element has the cross sectional area \( A_e = 3 \, mm^2 \) and leg length \( L_e = 2 \, mm \). Both
results are plotted in Figure 5.6. Both the temperature distributions are very close. On the other
hand, the heat flow rates show a slight discrepancy. Since we know the heat flow rate at the hot
junction and cold junction temperatures from the figure, we can calculate both the thermal
efficiencies using

\[
\eta_{th} = \frac{q(0) - q(L)}{q(0)}
\]

where \( q \) is the heat flow rate as a function of element distance \( x \). The calculated thermal
efficiencies for the exact solution and the ideal equation are \( \eta_{th} = 8.6 \% \) and \( \eta_{th} = 9.1 \% \),
respectively. This shows that the ideal equation solution with the material properties at a constant
average temperature has about 6 \% of larger efficiency than that of the exact solution for the
range of temperature of 400 K – 800 K.
Figure 5.6 Temperature profiles and heat flow rates for a thermoelectric generator at the matched load along the distance for the exact solution and the ideal equation. The following inputs are used: $T_h = 800$ K, $T_c = 400$ K, $A_e = 3 \text{mm}^2$, and $L_e = 2 \text{mm}$ (this work). The material properties in Figure 5.5 were evaluated at the mid-temperature of 600 K for the ideal equation.

5.2.3 Thermoelectric Coolers

In this section, the subscript 1 and 2 denote low and high quantities, respectively, such as $T_1 = T_c$ and $T_2 = T_h$ in Figure 5.4. The material properties for bismuth telluride is shown in Figure 5.11 [10].
Figure 5.7 Cures fitted from experimental data for bismuth telluride [10], (a) Seebeck coefficient, curve fit: $\alpha(T) = (-103.02 + 1.4882T - 0.0017T^2) \times 10^{-6} \, V/K$, (b) thermal conductivity, $k(T) = (3.2425 - 0.017T + 1.5 \times 10^{-5}T^2) \, W/mK$, (c) electrical conductivity, $\sigma(T) = (4105.5 - 13.211T + 0.0121 \, T^2) \times 100 \, (\Omega m)^{-1}$, $\rho(T) = 1/\sigma(T)$ and (d) dimensionless figure of merit.

The computations for the exact solution and the ideal equation for a thermoelectric cooler with the temperature-dependent material properties for bismuth telluride were conducted. The high and low junction temperatures are maintained as $T_1 = 408 \, K$ and $T_2 = 438 \, K$, respectively. The thermoelectric element has the cross sectional area $A_e = 1 \, mm^2$ and leg length $L_e = 1.5 \, mm$. The temperature and heat flow profiles for both are plotted in Figure 5.12, which shows somewhat
unexpected results. The temperature profile for the ideal equation appears lower than that of the exact solution, which results in a considerable lower heat flow rate.

![Temperature profiles and heat flow rates for a thermoelectric cooler](image)

Figure 5.8 Temperature profiles and heat flow rates for a thermoelectric cooler at a current of 1.3 A along the distance for the exact solution and the ideal equation. The following inputs are used: $T_1 = 408$ K, $T_2 = 438$ K, $A_e = 1 \text{ mm}^2$, and $L_e = 1.5 \text{ mm}$ (this work). The material properties for the ideal equation in Figure 5.11 were evaluated at an average temperature.

The coefficient of performance $COP$ can be calculated from

$$COP = \frac{q(0)}{q(L) - q(0)} \quad (5.29)$$

The calculated $COP$s for the exact solution and the ideal equation are $COP = 1.6$ and $COP = 1.34$, respectively. The ideal equation with material properties at a constant average temperature underestimates the $COP$ by about 17\% compared to the exact solution for a temperature difference of $\Delta T = 30$ K at current of $I = 1.3$ A. There are a number of reports in the literature about the Thomson effect which is only the effect of the temperature dependence of the Seebeck
coefficient. However, the exact solution includes all the material properties: Seebeck coefficient, electrical resistance, and thermal conductivity. It is interesting to note that the underestimate due to the temperature dependency of material properties usually offsets the losses by thermal and electrical contact resistances between thermoelements and ceramic and conductor plates.

We have studied the departure of the ideal equation for both thermoelectric generator and cooler from the exact solution. Further studies are encouraged from this starting point.

5.3 Compatibility Factor

Consider the one dimensional, steady state, thermoelectric power generation problem, where only a single element is considered. The following is based on the work of Snyder and Ursell (2003) [11, 12]. Note that the coordinate $x$ in Figure 5.9 is consistent with the previous chapters but opposite in sign to the original work of Snyder and Ursell. Hence, care should be taken that the expressions in this section may appear different from those in the original work, especially in sign not in quantity. The core reason of the present coordinate system is that we can use the equations developed in the previous chapters without changing the signs.

Figure 5.9 Diagram of a single element thermoelectric generator.
The electric current density \( j \) for a simple generator is given by

\[
j = \frac{I}{A_e}
\]  

(5.30)

From Equation (5.78), the electric field at any position is rewritten as

\[
\tilde{E} = \tilde{j} \rho + \alpha \tilde{\nabla} T
\]  

(5.31)

From Equation (5.91), the heat flux (heat flow density) is rewritten as

\[
\tilde{q} = \alpha \tilde{t} \tilde{j} - k \tilde{\nabla} T
\]  

(5.32)

From Equation (5.83), the electrical power density is rewritten as

\[
\dot{q} = \tilde{E} \cdot \tilde{j} = j^2 \rho + \tilde{j} \cdot \alpha \tilde{\nabla} T
\]  

(5.33)

From Equation (5.93), the heat balance equation is rewritten by

\[
\tilde{\nabla} \cdot (k \tilde{\nabla} T) + j^2 \rho - T \frac{d\alpha}{dT} \tilde{j} \cdot \tilde{\nabla} T = 0
\]  

(5.34)

**Reduced Current Density**

For the thermoelectric element in Figure 5.9, the reduced current density \( u \) can be defined as the ratio of the electric current density to the heat flux by conduction.[11]

\[
u \equiv \frac{j}{k \tilde{\nabla} T}
\]  

(5.35)

The sign of \( u \) requires caution. In order to have a positive value of \( u \) in Figure 5.9, \( j \) must be negative in direction since \( \nabla T \) is negative, which means that \( \alpha \) must be \( n \)-type material. However, \( p \)-type material can be dealt with just by switching the sign of \( \alpha \) to minus. For a
constant \( k \nabla T \), we can see that \( u \) is simply a scaled version of the current density \( j \). Using Equations (5.34) and (5.35), we have

\[
\frac{d \left( \frac{1}{u} \right)}{dT} = T \frac{d \alpha}{dT} - \rho ku
\]

(5.36)

**Heat Balance Equation**

The heat balance equation in terms of the reduced current density \( u \) is finally expressed as

\[
\frac{du}{dT} = -u^2 T \frac{d \alpha}{dT} + \rho ku^3
\]

(5.37)

which is not readily solved for \( u \).

**Numerical Solution**

A numerical solution for Equation (5.37) was developed by Snyder [13]. Equation (5.37) can be approximated by combining the zero Thomson effect (\( d\alpha/dT = 0 \)) solution and the zero resistance (\( \rho k = 0 \)) solution. For \( d\alpha/dT = 0 \) solution, the equation becomes

\[
\frac{du}{dT} = \rho ku^3
\]

(5.38)

If we integrate both sides, we have

\[
\int_{u_e}^{u} \frac{du}{u^3} = \int_{T_e}^{T} \rho k dT
\]

(5.39)

which leads to
\[
\frac{1}{u} = \frac{1}{u_c} \sqrt{1 - 2u^2 \bar{\rho}k(T - T_c)} \tag{5.40}
\]

where \(\bar{\rho}k\) denotes the average of \(\rho k\) between \(T\) and \(T_c\). For the zero resistance (\(\rho k = 0\)) solution, Equation (5.37) becomes

\[
\frac{du}{dT} = -u^2 T \frac{d\alpha}{dT} \tag{5.41}
\]

In a similar way, solving for the reduced current density,

\[
\frac{1}{u} = \frac{1}{u_c} + \bar{T}(\alpha - \alpha_c) \tag{5.42}
\]

Combining Equation (5.40) and (5.42) gives

\[
\frac{1}{u} = \frac{1}{u_c} \sqrt{1 - 2u^2 \bar{\rho}k(T - T_c)} + \bar{T}(\alpha - \alpha_c) \tag{5.43}
\]

In a discrete form of numerical solution for \(n\) and \(n - 1\) (across an infinitesimal layer), we have for \(n\)-type material

\[
\frac{1}{u_n} = \frac{1}{u_{n-1}} \sqrt{1 - 2u^2_n \bar{\rho}k(T_n - T_{n-1})} + \bar{T}(\alpha_n - \alpha_{n-1}) \tag{5.44}
\]

For \(p\)-type material, we have

\[
\frac{1}{u_n} = \frac{1}{u_{n-1}} \sqrt{1 - 2u^2_n \bar{\rho}k(T_n - T_{n-1})} - \bar{T}(\alpha_n - \alpha_{n-1}) \tag{5.45}
\]

This can be used to compute the reduced current density \(u(T)\) as a function of temperature with an initial \(u_i\). A specific initial \(u_i\) could be obtained for a maximum efficiency using Equations (5.44) and (5.61).
**Infinitesimal Efficiency**

Consider an infinitesimal layer of thickness $dx$. The infinitesimal efficiency $\eta$ is

$$\eta = \frac{\dot{q} dA_e}{q A_e} = \frac{\text{Power output}}{\text{Heat absorbed}}$$  \hspace{1cm} (5.46)

**Reduced Efficiency**

Equation (5.46) can be further developed. The total efficiency $\eta$ in terms of $u$ is

$$\eta = \frac{dT u(\alpha + \rho ku)}{\alpha u - \frac{1}{T}}$$  \hspace{1cm} (5.47)

The $dT/T$ is recognizable as the infinitesimal Carnot efficiency.

$$\eta_c = \frac{dT}{T} = \frac{\Delta T}{T} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}$$  \hspace{1cm} (5.48)

**Reduced Efficiency**

So we define the reduced efficiency $\eta_r$ as

$$\eta = \eta_c \eta_r$$  \hspace{1cm} (5.49)

where

$$\eta_r = \frac{u(\alpha + \rho ku)}{\alpha u - \frac{1}{T}}$$  \hspace{1cm} (5.50)

or, equivalently, if $\alpha$ and $u$ are not zero, we have an expression for $n$-type material as
For p-type material, we have

\[
\eta_r = \frac{1 - u \frac{\alpha}{Z}}{1 + \frac{1}{\alpha u T}} \quad (5.52)
\]

Compatibility Factor

It is found in Equation (5.51) that there is a largest reduced efficiency between \( u = 0 \) and \( u = \frac{Z}{\alpha} \). Hence, taking the derivative of the reduced efficiency \( \eta_r \) with respect to the reduced current density \( u \) and setting it to zero gives a specific reduced current \( u \) that is called the compatibility factor \( s \). For n-type material,

\[
s = \frac{1 - \sqrt{1 + Z T}}{\alpha T} \quad (5.53)
\]

For p-type material,

\[
s = \frac{\sqrt{1 + Z T} - 1}{\alpha T} \quad (5.54)
\]

Replacing this in place of \( u \) in Equation (5.51) gives the maximum reduced efficiency \( \eta_{r,\text{max}} \) as

\[
\eta_{r,\text{max}} = \frac{\sqrt{1 + Z T} - 1}{\sqrt{1 + Z T} + 1} \quad (5.55)
\]

As a general rule, \( \eta_r(T) \) is significantly compromised when \( u \) deviates from \( s \) by more than a factor of two [11].
Segmented Thermoelements

In applications with large temperature differences such as solar thermoelectric generators, the segmented thermoelement, which consists of more than one material in a thermoelectric leg, is often considered because one material cannot have good efficiency or sustainability over the entire temperature range. The compatibility factor is then a measure of maximum suitability over the segmented materials since one current flows through the segmented thermoelement. The compatibility factor is a thermodynamic property essential for designing an efficient segmented thermoelectric device. If the compatibility factors differ by a factor of 2 or more, the maximum efficiency can in fact decrease by segmentation [11].

Table 5.1 Spread sheet Calculation of $p$-type Element Performance based on Snyder and Ursell (2003) [11, 13].

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Material</th>
<th>$\alpha$ (µV/K)</th>
<th>$\rho \times 10^{3}$ (Ωcm)</th>
<th>$k$ (W/mK)</th>
<th>ZT</th>
<th>$u$ (1/V)</th>
<th>$s$ (1/V)</th>
<th>$\eta_c$ (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>973</td>
<td>CeFe$_4$Sb$_3$</td>
<td>156</td>
<td>0.849</td>
<td>2.689</td>
<td>1.04</td>
<td>3.62</td>
<td>2.82</td>
<td>15.66</td>
<td>0.00</td>
</tr>
<tr>
<td>948</td>
<td>CeFe$_4$Sb$_3$</td>
<td>160</td>
<td>0.842</td>
<td>2.698</td>
<td>1.07</td>
<td>3.64</td>
<td>2.89</td>
<td>16.24</td>
<td>0.44</td>
</tr>
<tr>
<td>923</td>
<td>CeFe$_4$Sb$_3$</td>
<td>164</td>
<td>0.834</td>
<td>2.706</td>
<td>1.10</td>
<td>3.66</td>
<td>2.97</td>
<td>16.83</td>
<td>0.90</td>
</tr>
<tr>
<td>898</td>
<td>CeFe$_4$Sb$_3$</td>
<td>166</td>
<td>0.826</td>
<td>2.712</td>
<td>1.10</td>
<td>3.66</td>
<td>3.02</td>
<td>17.09</td>
<td>1.38</td>
</tr>
<tr>
<td>873</td>
<td>CeFe$_4$Sb$_3$</td>
<td>167</td>
<td>0.818</td>
<td>2.717</td>
<td>1.10</td>
<td>3.64</td>
<td>3.07</td>
<td>17.19</td>
<td>1.89</td>
</tr>
<tr>
<td>848</td>
<td>CeFe$_4$Sb$_3$</td>
<td>167</td>
<td>0.809</td>
<td>2.72</td>
<td>1.07</td>
<td>3.62</td>
<td>3.11</td>
<td>17.14</td>
<td>2.40</td>
</tr>
<tr>
<td>823</td>
<td>CeFe$_4$Sb$_3$</td>
<td>167</td>
<td>0.8</td>
<td>2.722</td>
<td>1.05</td>
<td>3.59</td>
<td>3.15</td>
<td>17.07</td>
<td>2.93</td>
</tr>
<tr>
<td>798</td>
<td>CeFe$_4$Sb$_3$</td>
<td>166</td>
<td>0.791</td>
<td>2.723</td>
<td>1.02</td>
<td>3.56</td>
<td>3.18</td>
<td>16.82</td>
<td>3.46</td>
</tr>
<tr>
<td>773</td>
<td>CeFe$_4$Sb$_3$</td>
<td>164</td>
<td>0.782</td>
<td>2.723</td>
<td>0.98</td>
<td>3.51</td>
<td>3.20</td>
<td>16.40</td>
<td>4.01</td>
</tr>
<tr>
<td>748</td>
<td>CeFe$_4$Sb$_3$</td>
<td>162</td>
<td>0.772</td>
<td>2.722</td>
<td>0.93</td>
<td>3.47</td>
<td>3.22</td>
<td>15.99</td>
<td>4.55</td>
</tr>
<tr>
<td>723</td>
<td>CeFe$_4$Sb$_3$</td>
<td>160</td>
<td>0.762</td>
<td>2.721</td>
<td>0.89</td>
<td>3.43</td>
<td>3.25</td>
<td>15.55</td>
<td>5.09</td>
</tr>
<tr>
<td>698</td>
<td>CeFe$_4$Sb$_3$</td>
<td>157</td>
<td>0.752</td>
<td>2.719</td>
<td>0.84</td>
<td>3.39</td>
<td>3.26</td>
<td>14.95</td>
<td>5.64</td>
</tr>
<tr>
<td>673</td>
<td>CeFe$_4$Sb$_3$</td>
<td>154</td>
<td>0.741</td>
<td>2.716</td>
<td>0.79</td>
<td>3.35</td>
<td>3.27</td>
<td>14.36</td>
<td>6.18</td>
</tr>
<tr>
<td>673</td>
<td>Zn$_2$Sb$_3$</td>
<td>200</td>
<td>3.118</td>
<td>0.637</td>
<td>1.36</td>
<td>3.73</td>
<td>3.97</td>
<td>21.08</td>
<td>6.18</td>
</tr>
<tr>
<td>648</td>
<td>Zn$_2$Sb$_3$</td>
<td>195</td>
<td>3.064</td>
<td>0.637</td>
<td>1.26</td>
<td>3.66</td>
<td>3.99</td>
<td>20.13</td>
<td>6.95</td>
</tr>
<tr>
<td>623</td>
<td>Zn$_2$Sb$_3$</td>
<td>191</td>
<td>3.008</td>
<td>0.632</td>
<td>1.20</td>
<td>3.61</td>
<td>4.05</td>
<td>19.40</td>
<td>7.73</td>
</tr>
<tr>
<td>598</td>
<td>Zn$_2$Sb$_3$</td>
<td>187</td>
<td>2.949</td>
<td>0.622</td>
<td>1.14</td>
<td>3.55</td>
<td>4.14</td>
<td>18.74</td>
<td>8.50</td>
</tr>
<tr>
<td>573</td>
<td>Zn$_2$Sb$_3$</td>
<td>182</td>
<td>2.889</td>
<td>0.61</td>
<td>1.08</td>
<td>3.50</td>
<td>4.23</td>
<td>17.95</td>
<td>9.27</td>
</tr>
</tbody>
</table>
A segmented element with three materials, Bi$_2$Te$_3$, Zn$_4$Sb$_3$, and CeFe$_4$Sb$_3$ is examined. The three thermoelectric material properties along with temperature are listed in Table 5.1. The reduced current density $u$, compatibility factors $s$, reduced efficiency $\eta_r$ and maximum reduced efficiency $\eta_{r,\text{max}}$ are computed numerically using Equations (5.44), (5.53), (5.50), and (5.55) with an initial $u_i = 3.6179$ that is a value corresponding to the maximum efficiency. The results are plotted in Figure 5.10. The reduced current density $u$, which was defined as the ratio of the current density $j$ to the heat flow density $k\nabla T$, is a numerical solution from the heat balance equation of Equation (5.37). The reduced current density remains almost constant over the temperature. However, the compatibility factor $s$, which is a value corresponding to the maximum reduced efficiency, shows the maximum potential of the material. So the discrepancy between $u$ and $s$ causes the decrease of the reduced efficiency, which is shown in Figure 5.10 (b). This should be a good way of selecting segmented materials.
Figure 5.10 (a) Variation of reduced current density with temperature for a typical thermoelectric generator. (b) Reduced efficiency compared to the maximum reduced efficiency. These plots are based on the work of Snyder (2006) [11, 13].
Thermoelectric Potential

From Equation (5.32), the thermoelectric potential Φ is defined as

$$\Phi = \frac{q}{j} = \alpha T - \frac{1}{u}$$ \hspace{1cm} (5.56)

Then,

$$q = j\Phi$$ \hspace{1cm} (5.57)

When we take derivative of Equation (5.56), using Equation (5.31) we find

$$E = \nabla \Phi$$ \hspace{1cm} (5.58)

From Equation (5.33), the electrical power density is expressed as

$$\dot{q} = E j = j \nabla \Phi$$ \hspace{1cm} (5.59)

From Equation (5.46), the infinitesimal efficiency η is developed as

$$\eta = \frac{\dot{q} dx}{q} = \frac{j \nabla \Phi dx}{j \Phi} = \frac{d\Phi}{dx} \frac{dx}{\Phi} = \frac{d\Phi}{dx} = \frac{\Phi_h - \Phi_c}{\Phi_h} = 1 - \frac{\Phi_c}{\Phi_h}$$ \hspace{1cm} (5.60)

Hence, the infinitesimal efficiency is

$$\eta = 1 - \frac{\Phi_c}{\Phi_h} = 1 - \frac{\alpha_c T_c - \frac{1}{u_c}}{\alpha_h T_h - \frac{1}{u_h}}$$ \hspace{1cm} (5.61)
Using Equation (5.51) and (5.56), we have

\[ \eta_r = T \frac{d\ln \Phi}{dt} \]  \hspace{1cm} (5.62)

Taking integral of Equation (5.62) gives

\[ \frac{\Phi_h}{\Phi_c} = \exp \left[ - \int_{T_c}^{T_h} \eta_r \frac{T}{d} dT \right] \]  \hspace{1cm} (5.63)

From Equation (5.61), the overall efficiency of a finite segment is given by

\[ \eta = 1 - \exp \left[ - \int_{T_c}^{T_h} \eta_r \frac{T}{d} dT \right] \]  \hspace{1cm} (5.64)

Now we want to obtain the total efficiency \( \eta \) when \( \alpha, \rho \) and \( k \) are constant with respect to temperature, the performance of a generator operating at maximum efficiency can be calculated analytically. The resulting maximum efficiency is given by

\[ \eta_{max} = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_c}{T_h}} \]  \hspace{1cm} (5.65)

This equation is the normally attained maximum conversion efficiency in Chapter 2 with assumption of the constant material properties.
5.4 Thomson Effects

Thermoelectric phenomena are useful and have drawn much attention since the discovery of the phenomena in the early nineteenth century. The barriers to applications were low efficiencies and the availability of materials. In 1821, Thomas J. Seebeck discovered that an electromotive force or potential difference could be produced by a circuit made from two dissimilar wires when one junction was heated. This is called the Seebeck effect. In 1834, Jean Peltier discovered the reverse process that the passage of an electric current through a thermocouple produces heating or cooling depended on its direction [14]. This is called the Peltier effect (or Peltier cooling). In 1854, William Thomson discovered that if a temperature difference exists between any two points of a current-carrying conductor, heat is either absorbed or liberated depending on the direction of current and material [3]. This is called the Thomson effect (or Thomson heat). These three effects are called the thermoelectric effects. Thomson also developed important relationships between the above three effects with the reciprocal relations of the kinetic coefficients (or sometimes the so-called symmetry of the kinetic coefficients) under a peculiar assumption that the thermodynamically reversible and irreversible processes in thermoelectricity are separable [3]. The relationship developed is called the Thomson (or Kelvin) relations. The necessity for the assumption remained an objection to the theory until the advent of the new thermodynamics [15-17]. The relationship was later completely confirmed by experiments to be essentially a consequence of the Onsager’s Reciprocal Principle in 1931 [4].

As supported by Onsager’s Principle, the Thomson relations provide a simple expression for Peltier cooling, which is the product of the Seebeck coefficient, the temperature at the junction, and the current. This Peltier cooling is the principal thermoelectric cooling mechanism. There are two counteracting phenomena, which are the Joule heating and the thermal conduction. The net cooling power is the Peltier cooling minus these two effects. Actually the Joule heating affects the thermal conduction and consequently the Peltier cooling is subtracted only by the thermal conduction. Expressing the net cooling power in terms of the heat flux vector $\vec{q}$ gives [18].
5.4.1 Formulation of Basic Equations

Onsager’s Reciprocal Relations

The second law of thermodynamics with no mass transfer in an isotropic substance provides an expression for the entropy generation.

\[ S_{\text{gen}} = -\int \frac{\partial Q}{T} \]  

Suppose that the derivatives of the entropy generation \( s_{\text{gen}} \) per unit volume with respect to arbitrary quantities \( x_i \) are quantities \( J_i \) [16, 19]

\[ -\frac{\partial s_{\text{gen}}}{\partial x_i} = J_i \]  

(5.67)

At maximum \( s_{\text{gen}} \), \( J_i \) is zero. Accordingly, at the state close to equilibrium (or close to maximum), \( J_i \) is small [15]. The entropy generation per unit time and unit volume is

\[ -\dot{s}_{\text{gen}} = -\frac{\partial s_{\text{gen}}}{\partial t} = \frac{\partial x_i}{\partial t} J_i \]  

(5.68)

We express \( \partial x_i/\partial t \) as \( X_i \). Then, we have

\[ -\dot{s}_{\text{gen}} = X_i J_i \]  

(5.69)

The \( X_i \) are usually a function of \( J_i \). Onsager [4] stated that if \( J_i \) were completely independent, we should have the relation, expanding \( X_i \) in the powers of \( J_i \) and taking only linear terms [18].
\[ X_i = \sum_j R_{ij} J_j \]  \hspace{1cm} (5.70)

where \( R_{ij} \) are called the kinetic coefficients. Hence, we have

\[-\dot{s}_\text{gen} = \sum_i X_i J_i \]  \hspace{1cm} (5.71)

The smallness of \( J_i \) in practice means the linear terms are sufficient. It is necessary to choose the quantities \( X_i \) in some manner, and then to determine the \( J_i \). The \( X_i \) and \( J_i \) are conveniently determined simply by means of the formula for the rate of change of the total entropy generation.

\[ \dot{S}_\text{gen} = -\int \sum_i X_i J_i dV > 0 \]  \hspace{1cm} (5.72)

For two terms, we have

\[ \dot{S}_\text{gen} = -\int [X_1 J_1 + X_2 J_2] dV > 0 \]  \hspace{1cm} (5.73)

And

\[ X_1 = R_{11} J_1 + R_{12} J_2 \]  \hspace{1cm} (5.74)

\[ X_2 = R_{21} J_1 + R_{22} J_2 \]  \hspace{1cm} (5.75)

One can assert that the kinetic coefficients are symmetrical with respect to the suffixes 1 and 2.

\[ R_{12} = R_{21} \]  \hspace{1cm} (5.76)

which is called the reciprocal relations.
Basic Equations
Let us consider a non-uniformly heated thermoelectric material. For an isotropic substance, the continuity equation for a constant current gives
\[ \nabla \cdot \mathbf{j} = 0 \]  
(5.77)

The electric field \( \mathbf{E} \) is affected by the current density \( \mathbf{j} \) and the temperature gradient \( \nabla T \). The coefficients are determined from Ohm’s law and the Seebeck effect \[7\]. The field is then expressed as
\[ \mathbf{E} = \mathbf{j} \rho + \alpha \nabla T \]  
(5.78)

where \( \rho \) is the electrical resistivity and \( \alpha \) is the Seebeck coefficient. Solving for the current density gives
\[ \mathbf{j} = \frac{1}{\rho} \left( \mathbf{E} - \alpha \nabla T \right) \]  
(5.79)

The heat flux \( \mathbf{q} \) is also affected by both the field \( \mathbf{E} \) and temperature gradient \( \nabla T \). However, the coefficients were not readily attainable at that time. Thomson in 1854 arrived at the Thomson relationship assuming that thermoelectric phenomena and thermal conduction are independent. Later, Onsager supported that relationship by presenting the reciprocal principle which was experimentally verified \[17\]. Here we derive the Thomson relationship using Onsager’s principle. The heat flux with arbitrary coefficients is
\[ \mathbf{q} = C_1 \mathbf{E} - C_2 \nabla T \]  
(5.80)

The general heat diffusion equation is
\[-\vec{\nabla} \cdot \vec{q} + \dot{q} = \rho c_p \frac{\partial T}{\partial t}\]  
(5.81)

For steady state, we have

\[-\vec{\nabla} \cdot \vec{q} + \dot{q} = 0\]  
(5.82)

where \(\dot{q}\) is expressed by [18]

\[\dot{q} = \vec{E} \cdot \vec{j} = J^2 \rho + J \cdot \vec{\alpha} \vec{\nabla} T\]  
(5.83)

Expressing Equation (5.66) with Equation (5.82) with the heat flux gradient \(\vec{\nabla} \cdot \vec{q}\) having a minus sign, the entropy generation per unit time will be

\[\dot{S}_{gen} = -\frac{2}{\rho} \frac{\partial \dot{Q}}{\partial T} = \int \frac{1}{T} (-\vec{\nabla} \cdot \vec{q} + \dot{q}) dV\]  
(5.84)

Using Equation (5.83), we have

\[\dot{S}_{gen} = \int \frac{\vec{E} \cdot \vec{j}}{T} - \int \frac{\vec{\nabla} \cdot \vec{q}}{T} dV\]  
(5.85)

The second term is integrated by parts, using the divergence theorem and noting that the fully transported heat does not produce entropy since the volume term cancels out the surface contribution [18]. Then, we have

\[\dot{S}_{gen} = -\int \left( \frac{-\vec{E} \cdot \vec{j}}{T} + \frac{\vec{q} \cdot \vec{\nabla} T}{T^2} \right) dV\]  
(5.86)

If we take \(\vec{j}\) and \(\vec{q}\) as \(X_1\) and \(X_2\), then the corresponding quantities \(J_1\) and \(J_2\) are the components of the vectors \(-\vec{E} / T\) and \(\vec{\nabla} T / T^2\) [18]. Accordingly, as shown in Equations (5.74) and (5.75) with Equation (5.80), we have
\[ \bar{j} = -\frac{1}{\rho} T \left( -\frac{\bar{E}}{T} \right) - \frac{1}{\rho} \alpha T^2 \frac{\bar{\nabla} T}{T^2} \]  

(5.87)

\[ \bar{q} = -C_T T \left( -\frac{\bar{E}}{T} \right) - C_T T^2 \frac{\bar{\nabla} T}{T^2} \]  

(5.88)

The reciprocal relations in Equation (5.76) give

\[ C_T = \frac{1}{\rho} \alpha T^2 \]  

(5.89)

Thus, we have \( C_1 = \alpha T / \rho \). Inserting this and Equation (5.78) and using (5.88) gives

\[ \bar{q} = \alpha T \bar{j} - \left( C_2 - \frac{\alpha^2 T}{\rho} \right) \bar{\nabla} T \]  

(5.90)

We introduce the Wiedemann-Franz law, \( L_o = k \rho / T \), where \( L_o \) is the Lorentz number (constant). Expressing \( k \) as \( L_o T / \rho \), we find that the coefficient \( \left( C_2 - \alpha^2 T / \rho \right) \) is nothing more than the thermal conductivity \( k \). Finally, the heat flow density vector (heat flux) is expressed as

\[ \bar{q} = \alpha T \bar{j} - k \bar{\nabla} T \]  

(5.91)

This is the most important equation for thermoelectric phenomena. The second term pertains to the thermal conduction and the term of interest is the first term, which gives the thermoelectric effects: directly the Peltier cooling but indirectly the Seebeck effect and the Thomson heat \([5, 19, 20] \). Inserting Equations (5.78) and (5.91) into Equation (5.86) gives
The entropy generation per unit time for the irreversible processes is indeed greater than zero since $\rho$ and $k$ are positive. Note that the Joule heating and the thermal conduction in the equation are indeed irreversible. This equation satisfies the requirement for Onsager’s reciprocal relations shown in Equation (5.73). Substituting Equations (5.83) and (5.91) in Equation (5.82) yields

$$\tilde{\nabla} \cdot \left( k \tilde{\nabla} T \right) + j^2 \rho - T \frac{d\alpha}{dT} \tilde{\nabla} \cdot \tilde{\nabla} T = 0 \quad (5.93)$$

The Thomson coefficient $\tau$, originally obtained from the Thomson relations, is written

$$\tau = T \frac{d\alpha}{dT} \quad (5.94)$$

In Equation (5.93), the first term is the thermal conduction, the second term is the Joule heating, and the third term is the Thomson heat. Note that if the Seebeck coefficient $\alpha$ is independent of temperature, the Thomson coefficient $\tau$ is zero and then the Thomson heat is absent.
Figure 5.11 Thermoelectric cooler with $p$-type and $n$-type thermoelements.

5.4.2 Numeric Solutions of Thomson Effect

Let us consider one of the $p$- and $n$-type thermoelements shown in Figure 5.11, knowing that $p$- and $n$-type thermoelements produce the same results if the materials and dimensions are assumed to be similar. Equation (5.93) for one dimensional analysis at steady state gives the non-linear differential governing equation as

\[
\frac{d^2 T}{dx^2} - \frac{I}{Ak} \frac{d\alpha}{dT} T \frac{dT}{dx} + \frac{I^2 \rho}{A^2 k} = 0
\]

where $A$ is the cross-sectional area of the thermoelement. We want to make it dimensionless. The boundary conditions will be $T(0) = T_1$ and $T(L) = T_2$. Then, Let

\[
\theta = \frac{T - T_1}{T_2 - T_1} \quad \text{and} \quad \xi = \frac{x}{L}
\]

where $L$ is the element length. Then, the dimensionless differential equation is

\[
\frac{d^2 \theta}{d\xi^2} - \beta ((\theta - 1)\phi + 1) \frac{d\theta}{d\xi} + \gamma = 0
\]

where the dimensionless numbers are defined as follows. The boundary condition will be that $\theta(0) = 0$ and $\theta(1) = 1$. Equation (5.97) was formulated on the basis of the high junction temperature $T_2$ to accommodate the commercial products.
\[
\beta = \frac{\int_{T_1}^{T_2} \frac{d\alpha}{dT} \Delta T}{Ak \frac{\Delta T}{L}}
\]  
(5.98)

where \(\beta\) is the ratio of the Thomson heat to the thermal conduction. Note that \(\beta\) is not a function of \(\Delta T\).

\[
\gamma = \frac{I^2R}{Ak \frac{\Delta T}{L}}
\]  
(5.99)

where \(\gamma\) is the ratio of the Joule heating to the thermal conduction.

\[
\phi = \frac{\Delta T}{T_2}
\]  
(5.100)

where \(\phi\) is the ratio of temperature difference to the high junction temperature. The temperature difference is

\[
\Delta T = T_2 - T_1
\]  
(5.101)

where \(\Delta T\) is the high junction temperature \(T_2\) minus the low junction temperature \(T_1\). Therefore, \(T_1\) is a function of \(\Delta T\) since \(T_2\) is fixed. The cooling power at the cold junction using Equation (5.91) is

\[
\dot{Q}_1 = \alpha(T_1)T_1 I + \left( -kA \left. \frac{dT}{dx} \right|_{x=0} \right)
\]  
(5.102)
where the first term is the Peltier cooling and the second term is the thermal conduction. It has been customary in the literature for the exact solution wherein the Seebeck coefficient \( \alpha \) is evaluated at the cold junction temperature \( T_1 \). The dimensionless cooling power is

\[
\Theta_1 = \Pi \left( \frac{1 - \phi}{\phi} \right) - \frac{d\theta}{d\xi} \bigg|_{\xi=0} \tag{5.103}
\]

where \( \Theta_1 \) is the dimensionless cooling power, which by definition is

\[
\Theta_1 = \frac{\dot{Q}_1}{Ak\Delta T/L} \tag{5.104}
\]

The dimensionless Peltier cooling is

\[
\Pi = \frac{\alpha(T_1)I}{Ak/L} \tag{5.105}
\]

The work per unit time is \( \dot{W} = \alpha d\Delta T + I^2 R \). Then the dimensionless work per unit time \( \Psi \) is expressed by

\[
\Psi = \Pi + \gamma \tag{5.106}
\]

where \( \Psi = \frac{\dot{W}}{Ak\Delta T/L} \). Then the coefficient of performance [21] for the thermoelectric cooler, determined as the cooling power over the work, is

\[
COP = \frac{\Theta_1}{\Psi} \tag{5.107}
\]
Equation (5.97) can be exactly solved for the temperature distributions with the mathematical software Mathcad and the cooling power of Equation (5.102) can be obtained. These are the exact solutions including the Thomson effect.

**Ideal Equation**

According to the assumption made by both the Thomson relations and Onsager’s reciprocal relations, the thermoelectric effects and the thermal conduction in Equation (5.91) are completely independent, which implies that each term may be separately dealt with. In fact, separately dealing with the reversible processes of the three thermoelectric effects yielded the Peltier cooling of the \( \alpha T I \) in the equation. Under the assumption that the Thomson coefficient is negligible or the Seebeck coefficient is independent of temperature, Equation (5.95) easily provides the exact solution of the temperature distribution. Then, Equation (5.102) with the temperature distribution for the cooling power at the cold junction reduces to

\[
\dot{Q}_1 = \alpha(T_{\text{avg}}) I_1 I - \frac{1}{2} I^2 R - \frac{\Delta k}{L} (T_2 - T_1) 
\]

which appears simple but is still a robust equation giving a usually good agreement with experiments and with comprehensive applications in science and industry. This is here called the *ideal equation*. The ideal equation assumes that the Seebeck coefficient \( \alpha \) is evaluated at the average of \( \Delta T \) [22, 23] as a result of the internal phenomena being imposed on the surface phenomena.
5.4.3 Comparison between Thomson Effect and Ideal Equation

In order to examine the Thomson effect on the temperature distributions with a temperature dependent Seebeck coefficient, a real commercial module of Laird CP10-127-05 was chosen. Both the temperature-dependent properties and the dimensions for the module were provided by the manufacturer, which are shown in Table 5.2 and the temperature-dependent Seebeck coefficient is graphed in Figure 5.12.

Table 5.2 Maximum values, Dimensions, and the Properties for a Commercial Module

<table>
<thead>
<tr>
<th>TEC Module (Laird CP10-127-05)</th>
<th>at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta T_{max}$ (°C)</td>
<td>67</td>
</tr>
<tr>
<td>$I_{max}$ (A)</td>
<td>3.9</td>
</tr>
<tr>
<td>$Q_{max}$ (W)</td>
<td>34.3</td>
</tr>
<tr>
<td>$L$ (mm), element length</td>
<td>1.253</td>
</tr>
<tr>
<td>$A$ (mm$^2$), cross-sectional area</td>
<td>1</td>
</tr>
</tbody>
</table>
To reveal the Thomson effect, only the Seebeck coefficients are considered to be dependent on the temperature while the electrical resistivity and the thermal conductivity are constant as shown in Table 5.2. In Figure 5.12, the Seebeck coefficient increases with increasing the temperature up to about 350 K and then decreases with increasing the temperature, so that there is a peak value. For the solution of the non-linear differential equation, linear fits for the Seebeck coefficient were used in the present work. In Figure 5.12, one linear fit to the first part for a range from 250 K to 350 K was used, while another linear fit of the second part for the range from 350 K to 450 K was used. The linear fits of the two parts are shown in Table 1.

The dimensionless differential equation, Equation (5.97), was developed on the basis of a fixed high junction temperature \( T_2 \) so that the low junction temperature \( T_1 \) decreases as \( \Delta T \) increases. \( \beta \) in Equation (5.98) is the dimensionless number indicating approximately the ratio of the Thomson heat to the thermal conduction. \( \beta \) is a function only of the slope \( d\alpha/dT \) and the current \( I \). Equation (5.97) with the given boundary conditions was solved for the temperature distributions using Mathcad.

A typical value of \( \beta = 0.2 \) was used for the commercial product at \( T_2 = 298 \) K and \( I_{\text{max}} = 3.9 \) A. And a hypothetical value of \( \beta = 1.0 \) that is fivefold larger than the typical value of 0.2 was used in order to closely examine the Thomson effect. \( \gamma \) in Equation (5.99) is the dimensionless number indicating approximately the ratio of the Joule heating to the thermal conduction.

<table>
<thead>
<tr>
<th># of Thermocouples</th>
<th>127</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha(T), (\mu V/K) )</td>
<td>0.2068T+138.78, 250 K &lt; T &lt; 350 K</td>
</tr>
<tr>
<td>( \alpha(T), (\mu V/K) )</td>
<td>-0.2144T+281.02, 350 K &lt; T &lt; 450 K</td>
</tr>
<tr>
<td>( \rho (\Omega \text{cm}) ) at 27 ( ^\circ )C</td>
<td>( 1.01 \times 10^{-3} )</td>
</tr>
<tr>
<td>( k (\text{W/cmK}) ) at 27 ( ^\circ )C</td>
<td>( 1.51 \times 10^{-2} )</td>
</tr>
<tr>
<td>Module size</td>
<td>( 30 \times 30 \times 3.2 ) mm</td>
</tr>
</tbody>
</table>
Figure 5.13 shows the temperature distributions at $T_2 = 298$ K and $I = 3.9$ A as a function of $\xi$ along with $\beta$ for $\Delta T = 10$ K ($\gamma = 15.97$). The Joule heating appears dominant with a such high value of $\gamma = 15.97$. For the commercial cases with $\beta = 0.2$, the Thomson effects appear small compared to the Ideal Equation at $\beta = 0$. The hypothetical cases at $\beta = 1.0$ obviously provide salient examples for the Thomson effect. Since the temperature gradient at $\xi = 0$ counteracts the Peltier cooling, the slightly lower temperature distribution near zero acts as improving the net cooling power. The Thomson heat is effectively described by the product of $\beta$ and $d\theta/d\xi$. Suppose that we think of a $p$-type thermoelement (no difference with $n$-type). The current flows in the positive direction. The Thomson heat acts as liberating heat when the $\beta d\theta/d\xi$ is positive, while it acts as heat absorbing when the $\beta d\theta/d\xi$ is negative. In the first half of the temperature distribution, both $\beta$ and $d\theta/d\xi$ are positive, so that the product is positive. It is known that the moving charged electrons or holes transport not only the electric energy but also the thermal energy as absorbing and liberating, depending on the sign of $\beta d\theta/d\xi$, along the thermoelement. The temperature distribution is slightly shifted forward giving the lower temperature distribution near $\xi = 0$ which results in the improved cooling power at the cold junction.

The net cooling power $\dot{Q}_1$ in Equation (5.102) and the coefficient of performance $COP$ [21] in Equation (5.107) along the current at $T_2 = 298$ K (thin lines) for $\Delta T = 10$ K are presented in Figure 5.14. The maximum current for this commercial module is 3.9 A as shown in Table 1, so the operating current barely exceeds the maximum current in practice. The slight improvement by the Thomson effect on $\dot{Q}_1$ at 298K is also reflected on the corresponding $COP$. 
Figure 5.13 For $\Delta T = 10$ K ($\gamma = 15.97$), dimensionless temperature $\theta$ vs. dimensionless distance $\xi$ as a function of $\beta$. The operating conditions are $T_2 = 298$ K and $I = 3.9$ A.
Figure 5.14 Cooling power and COP vs. current at $T_2 = 298$ K and 420 K for $\Delta T = 10$ K. $\beta = -0.29$ at $T_2 = 420$ K and $\beta = 0.2$ at $T_2 = 298$ K[24]

**Problems**

5.1. Derive Equation (5.91) and (5.93) in detail.
5.2. Describe the Thomson heat.
5.3. What is the Thomson relations?
5.4. Derive Equations (5.22) and (5.23) of the exact solutions and explain what is the meaning of the exact solution.
5.5. Derive Equations (5.26) and (5.27) of the ideal equation and explain what is the meaning of the ideal equation.
5.6. Derive in detail Equation (5.53).
5.7. Derive in detail Equation (5.55).

**Projects**

5.8. Develop a Mathcad program to provide Figure 5.6 for a thermoelectric generator and explore the disagreement of the ideal equation comparing with the exact solution.
5.9. Develop a Mathcad program to provide Figure 5.8 for a thermoelectric cooler and explore the disagreement of the ideal equation comparing with the exact solution.
References


