Peltier's and Thomson's coefficients of thermoelectric phenomena in the observable

formulation

# Peltier's and Thomson's coefficients of thermoelectric phenomena in the observable formulation

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## Abstract

Four transport coefficients characterize the thermoelectric properties of materials. Three of them are widely measured and studied. But the number of references on the Peltier coefficient are very limited. This unequal result is a consequence of the Onsager reciprocal relation (ORR). A review on the preciseness and accuracy of Peltier coefficient measurements has been developed in this paper. Thus we can appreciate a low level in the experimental confirmation for the ORR. In order to describe the thermoelectric processes in an advantageous way, the observable formulation has been used. This is characterized by the electric potential measured at the probe terminals and for the heat flux which the conductor laterally dissipates. The energy balance provides the basic relationships among the observables and the Peltier and Thomson coefficients. A new way for measuring the Peltier coefficient has been suggested.

## 1. Introduction

Four transport coefficients characterize the thermoelectric properties of materials: the thermal conductivity $\kappa$, the thermoelectric power or Seebeck coefficient $S$, the electric conductivity $\sigma$ and the Peltier coefficient $\pi$. The first three are widely measured and studied: dozens of papers are published every year. Nevertheless, for the last coefficient the number of references is very limited: they do not average a paper a year. In this unequal result the Onsager reciprocal relation (ORR) $\pi = TS$ has a decisive influence. In fact, the easiness and accuracy of the techniques which measure the Seebeck coefficient obviates the need for Peltier coefficient measurements. But the ORR, which is founded in statistical mechanics, needs to be experimentally checked in a few cases at least. Therefore the experimental confirmation of this relation depends on the preciseness and accuracy of Peltier coefficient measurements [1–7]. A review of this subject has been developed in this work.

In order to describe the thermoelectric processes in an advantageous way, the observable formulation has been used [8]. This is characterized by the electric potential measured at the probe terminals and for the heat flux which the conductor laterally dissipates. In this formulation both the electrochemical potential of the electrons and the energy flux play the central role. The energy balance provides the basic relationships among the observables and the Peltier and Thomson coefficients.

The interest in studying the Peltier coefficient is also due to the fact this coefficient forms part of the expressions which define both the Thomson coefficient $\tau$ and the figure of merit $ZT$. The first combines the effect of two basic coefficients $\tau = \mathrm{d}\pi/\mathrm{d}T - S$, while the second relates three of them: $ZT = \sigma\pi^2/T\kappa$. When one applies the ORR, we deduce the well-known expressions $\tau = T(\mathrm{d}S/\mathrm{d}T)$ and $ZT = \sigma S^2 T/\kappa$. The first provides the bases to evaluate $\mathrm{d}S/\mathrm{d}T$ from measurements of Thomson's coefficient [9] and the second is relevant to technological questions of great importance, such as the construction of solid state energy conversion devices. Materials with high thermoelectric figures of merit are promising candidates for use in thermoelectric power generation.

## 2. Theory

### 2.1. Transport equations

The evaluation of the transport coefficients is carried out in filiform systems from the measurement of several observables. In these wires all the flows and forces are parallel to the $x$ direction. The transport equations of the thermoelectric phenomena are usually expressed in a local

$$J_U = \kappa A \frac{dT}{dx} + \left( \pi - \frac{\tilde{\mu}_e}{e} \right) I \qquad (1)$$

$$\frac{d(\tilde{\mu}_e/e)}{dx} = S \frac{dT}{dx} - \frac{1}{\sigma A} I \qquad (2)$$

where $J_U$ is the energy flux, $A$ is the cross-sectional area, $\tilde{\mu}_e$ is the electrochemical potential of the electron, $e > 0$ is the magnitude of the electron charge and $I$ is the electric current. Here, the positive direction of the fluxes $J_U$ and $I$ is the opposite of the coordinate $x$ (figure 1).

To evaluate the transport coefficients of a material we need to know the local values of the following quantities: $J_U$, $T$, $\tilde{\mu}_e$ and $I$. Some of them can be directly measured, i.e. $T$ and $I$. The other quantities need to be determined from the observable electric potential $\Delta \psi = \psi^{II} - \psi^{I}$ measured between the terminals of probes Z connected to sections I and II, and the heat flux $J_Q$ which laterally departs from the conductor towards the surroundings between sections I and II (figure 1). These two observables are defined next.

### 2.2. Observable electric potential

The observable electric potential $\psi$ measured at the terminals of probes Z at a temperature $T_o$ is closely related to the distribution of the electrochemical potential $\tilde{\mu}_e$ of the electrons along the conductor. In an element $dx$ the change in temperature and in electrochemical potential of the electrons is $dT$ and $d\tilde{\mu}_e$, respectively. The quantity $d\tilde{\mu}_e$ can be split in two terms [8]:

$$d\tilde{\mu}_e = (d\tilde{\mu}_e)_Z + (d\tilde{\mu}_e)_{volt}. \qquad (3)$$

The first can be expressed through the Seebeck coefficient of the probes, that is $(d\tilde{\mu}_e)_Z = eS_Z \, dT$, and the second is measured by a voltmeter, that is $(d\tilde{\mu}_e)_{volt} = -e \, d\psi$ [12, 13]. Then, we have

$$d(\tilde{\mu}_e/e) = S_Z \, dT - d\psi, \qquad (4)$$

and the second transport equation, equation (2), can be transformed into

$$\frac{d\psi}{dx} = (S_Z - S_X) \frac{dT}{dx} + \frac{1}{\sigma A} I. \qquad (5)$$

When the probes are of the same material as the conductor, that is Z ≡ X, equation (5) simplifies to $d\psi = I \, dR$, where $dR = dx/\sigma A$ is the electric resistance of the element $dx$ of conductor X. That is, when Z ≡ X the observable electric potential difference measures the ohmic drop independently of the actual temperature distribution in the conductor.

### 2.3. Energy balance

Under steady-state conditions, and for the wire geometry considered here, the energy balance in the wire between two cross sections I and II is presented as $J_U^{II} - J_U^{I} = J_Q$, where $J_Q$ is the heat flux that laterally departs between sections I and
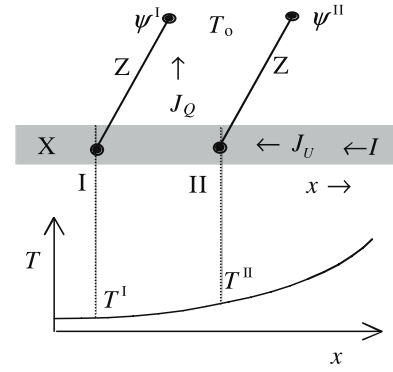


**Figure 1.** Observables $\Delta \psi = \psi^{II} - \psi^{I}$ and $J_Q$ in conductor X. The terminals of probes Z are at the same temperature $T_o$.

II from the wire to the surroundings (figure 1). From the result $J_U^{II} - J_U^{I} = J_Q$ and equation (1) we obtain

$$\Delta \left( \kappa A \frac{dT}{dx} \right) + I \Delta \pi - I \Delta \left( \frac{\tilde{\mu}_e}{e} \right) = J_Q, \qquad (6)$$

which can be used to evaluate the Peltier and Thomson coefficients.

### 2.4. Single wire

When $I = 0$, from equation (5) we have

$$S_Z - S_X = \left( \frac{\partial \Delta \psi}{\partial T^{II}} \right)_{T^I, I=0}. \qquad (7)$$

This expression is commonly used to evaluate $S_Z - S_X$. Note that only differences can be determined but not their absolute values. In these measurements four leads are attached to the sample in order to provide the values of $\Delta \psi$, $T^I$ and $T^{II}$ [14, 15].

To evaluate the Thomson coefficient $\tau = d\pi/dT - S$ we consider two sections I and II in a conductor X at different temperatures $T^I \neq T^{II}$ (figure 1). If the probes and wire are of the same material, Z ≡ X, equation (4) can be integrated as $\Delta \tilde{\mu}_e/e = \int_{T^I}^{T^{II}} S \, dT - \Delta \psi$. Combining this result and equation (6) we find the energy balance

$$\Delta \left( \kappa A \frac{dT}{dx} \right) + I \int_{T^I}^{T^{II}} \tau \, dT + I \Delta \psi = J_Q, \qquad (8)$$

that allows us to evaluate the Thomson coefficient from the observables $dT^I/dx$, $dT^{II}/dx$, $\Delta \psi = RI$ and $J_Q$.

### 2.5. Couple X/Y

Consider a couple X/Y (figure 2) where an electric current $I$ is flowing. The temperature distribution evolves towards a steady state with a maximum (or a minimum) at the junction. The energy balance at the junction is expressed by $(J_U)_X \equiv (J_U)_Y$, where the subscripts X and Y denote each of the two wires. The equilibrium for the distribution of matter at the junction
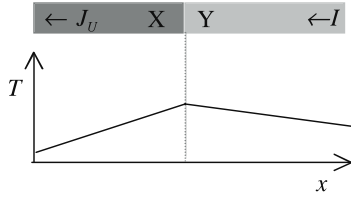
**Figure 2.** Peltier's effect refers to the temperature profile along a couple X/Y. At the steady state the junction temperature reaches a maximum (or a minimum).

is expressed by $(\tilde{\mu}_e)_X = (\tilde{\mu}_e)_Y$. Then, from equation (1) we deduce $(\pi_Y - \pi_X)I = A[\kappa_X(dT_X/dx) - \kappa_Y(dT_Y/dx)]$ and we can evaluate the Peltier coefficient from measurement of the two temperature gradients in the junction region. As far as we know, the difference in Peltier coefficients has never been measured using this equation.

The usual way of determining $\Delta\pi = \pi_Y - \pi_X$ considers the couple at a steady state while an electric current $I$ is flowing (figure 3). Let I and II be two sections at the same temperature $T = T^I = T^{II}$. Then, as $\Delta(\tilde{\mu}_e/e) = -\Delta\psi$, equation (6) can be written

$$\Delta\left(\kappa A \frac{dT}{dx}\right) + I\Delta\pi + I\Delta\psi = J_Q. \quad (9)$$

Therefore from the observables $dT^I/dx$, $dT^{II}/dx$, $\Delta\psi$ and $J_Q$ we can calculate $\Delta\pi = \pi_Y - \pi_X$. This energy balance can also be expressed in terms of the electric resistance

$$\Delta\left(\kappa A \frac{dT}{dx}\right) + I\Delta\pi + RI^2 + I\int_{T^I}^{T^{II}}(S_Y - S_X)\,dT = J_Q, \quad (10)$$

where $R = R_X + R_Y$, $R_X = \int_{x^I}^{x^{III}} dx/\sigma_X A_X$ and $R_Y = \int_{x^{III}}^{x^{II}} dx/\sigma_Y A_Y$.

## 3. Review of experimental work

In section 2 several expressions that relate the transport coefficients with the observables $\Delta\psi$ and $J_Q$ have been deduced. Some of them are well known and have been successfully applied for evaluating transport coefficients, as in thermal conductivity $\kappa$, thermoelectric power $S$ and electric conductivity $\sigma$ [16, 17]. However we cannot say the same when we refer to Peltier and Thomson coefficients. In the literature we find work where other energy balances have been applied. Then a critical review is needed.

### 3.1. Peltier's coefficient

The direct measurements of the Peltier coefficient are usually based on energy balances. This makes them difficult and rare [18]. In fact, we find very few works with measurements on this coefficient. Some of these papers use couples X/Y and apply the energy balance under steady-state isothermal conditions. Then, the Fourier term $\Delta[\kappa A(dT/dx)]$ and the Seebeck term $I\int_{T^I}^{T^{II}}(S_Y - S_X)\,dT$ of equation (10) disappear.
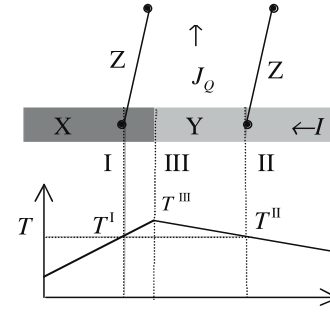


**Figure 3.** To determine $\pi_Y - \pi_X$ the observables $dT^I/dx$, $dT^{II}/dx$, $\Delta\psi$, and $J_Q$ need to be measured. Sections I and II have the same temperature $T^I = T^{II}$.
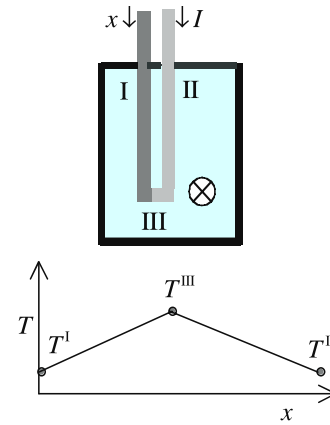


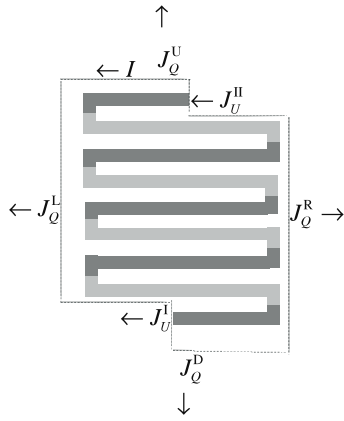**Figure 4.** Scheme of the device used by Caswell [1]. The couple Cu/Bi has been introduced in a calorimeter. Cu: dark line; Bi: light line. ⊗ stirrer.

But this temperature distribution does not seem to be possible because at the junction $dT_X/dx \neq dT_Y/dx$ due to $\pi_X \neq \pi_Y$ (see figure 2). This subject will be discussed in the following review of several selected papers.

Caswell [1] introduced a couple Cu/Bi in a calorimeter (figure 4) and assumed the energy balance typical of an isothermal system $(\pi_{Bi} - \pi_{Cu})I + RI^2 = J_Q$, where the Fourier and the Seebeck terms have not been considered. Now we can estimate the weight of these terms for a very smooth linear temperature profile with $T^{III} - T^I = 0.1$ K and $T^I = T^{II}$ (see figure 4). Thus we obtain $\Delta[\kappa A(dT/dx)] = -13$ mW and $I\int_{T^I}^{T^{II}}(S_{Bi} - S_{Cu})\,dT \approx 5.7\ \mu$W. The Fourier term is of the same order of magnitude as the Peltier term $(\pi_{Bi} - \pi_{Cu})I = 17$ mW and the Seebeck term is negligible. Therefore we conclude that measurements of $dT^I/dx$ and $dT^{II}/dx$ are needed to obtain accurate Peltier coefficients. In these calculations the following data reported in this paper have been used [1]: $I = 1.037$ A, $A_{Cu} = 48$ mm$^2$, $A_{Bi} = 36$ mm$^2$, $\kappa_{Cu} = 400$ W m$^{-1}$ K$^{-1}$, $\kappa_{Bi} = 7.97$ W m$^{-1}$ K$^{-1}$, $S_{Bi} - S_{Cu} = 54.8\ \mu$V K$^{-1}$, $\pi_{Bi} - \pi_{Cu} = 16$ mV and $x^{III} - x^I = x^{III} - x^{II} = 15$ cm.

Rötzer et al [2] measured the Peltier coefficient at the solid(S)–liquid(L) interface of highly doped p-type silicon. Initially, an AC current is used. When the temperature was uniform and constant, the current was changed to direct mode,
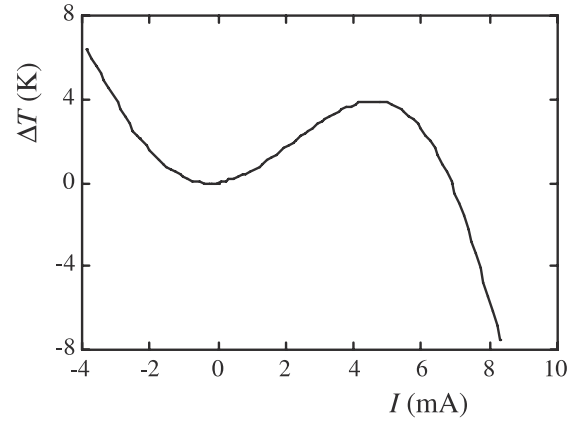
**Figure 5.** Scheme of the thermopile [3]. Ni: dark line; Pt: light line.



**Figure 6.** An estimation of the values $\Delta T = T^{III} - T^{I}$ with respect to the current $I$ in a couple Co/Au. A scheme of the system is given in figure 3. Data from Fukushima *et al* [4].

maintaining the same Joule's heating. Then the solid phase was fused and the interface was moved. From the value of this velocity they could evaluate the junction Peltier coefficient $\pi^{L} - \pi^{S}$ from the energy balance and equation (1). In order to apply the initial conditions they worked in very short times, less than 10 ms. The system had to remain in an isothermal state to avoid Fourier terms. Although this kind of interface has a limited interest, the work could be used in order to check the ORR. But nothing can be said about this relationship because the authors did not measure the Seebeck coefficient $S^{L} - S^{S}$.

Jiménez *et al* [3] designed a thermopile made of couples Ni/Pt (figure 5) and considered the heat fluxes from the thermopile in four spatial directions, $J_{Q}^{U}$, $J_{Q}^{R}$, $J_{Q}^{D}$ and $J_{Q}^{L}$. If we apply the energy balance to the four couples between sections I and II in figure 5, since $T^{I} = T^{II}$, $dT^{I}/dx = dT^{II}/dx$ and $\pi_{Ni}^{I} = \pi_{Ni}^{II}$, we deduce from equation (9) that $I\Delta\psi = J_{Q}^{U} + J_{Q}^{R} + J_{Q}^{D} + J_{Q}^{L}$. That is, the measured values of the heat fluxes can only provide information on the electric power dissipation. However, these authors claimed to have found a relation between the junction Peltier coefficient $\pi_{Pt} - \pi_{Ni}$ and the heat fluxes $J_{Q}^{L}$ and $J_{Q}^{R}$.

Fukushima *et al* [4] evaluated the Peltier coefficient in a couple Co/Au. They measured the apparent electric resistance $R_{app} = \Delta\psi/I$ and found that the $R_{app} \propto I$ curve had a parabolic shape. Then they assumed that, for a certain electric current $I_{P}$, the Peltier heat flux may be exactly balanced by the Joule power $R(I_{P})^{2} + (\pi_{Au} - \pi_{Co})I_{P} = 0$, as it occurs in an isothermal system. But this kind of temperature distribution is not possible and therefore the Fourier and Seebeck terms might have a non-negligible weight. In the following we are going to estimate these terms.

We assume a linear temperature profile as in figure 3. First we calculate the value of $\Delta T = T^{III} - T^{I}$ for every current. From $\Delta\psi = \int_{T^{I}}^{T^{II}} (S_{Au} - S_{Co}) dT + IR$ we deduce $R_{app} = (S_{Au} - S_{Co})\Delta T/I + R$ and therefore $\Delta T = (R_{app} - R_{0})I/(k_{Co/Au}I + (S_{Au} - S_{Co}))$, where $R_{0}$ is the zero current resistance. With the data reported in [4], $R_{app}$ in figure 2(a), $R_{0} = 3.6\ \Omega$, $R = R_{0} + k_{Co/Au}\Delta T$, $k_{Co/Au} = (1/2)(dR_{0}/dT) = 2.75 \times 10^{-3}\ \Omega\ K^{-1}$ and $S_{Au} - S_{Co} = 3.288 \times 10^{-5}\ V\ K^{-1}$, we deduce the correlation $\Delta T \propto I$ shown in figure 6. These values are in agreement with the

maximum decrement of temperature for the couple Co/Au, which Fukushima *et al* [4] estimated at 4.6 K.

Finally we can evaluate the Fourier, Seebeck and Peltier terms of the energy balance given by equation (10). For $I = 8.3$ mA we obtain $\Delta[\kappa A(dT/dx)] = 220\ \mu W$, $I\int_{T^{I}}^{T^{II}} (S_{Au} - S_{Co}) dT = -2\ \mu W$ and $I(\pi_{Au} - \pi_{Co}) = 220\ \mu W$. We can see that the Fourier term has the same order of magnitude as the Peltier term and therefore it cannot be considered as a negligible quantity. In these calculations we use the data reported by Fukushima *et al* [4], $A = 70 \times 200$ nm$^{2}$, $\Delta x_{Au} = 220$ nm, $\Delta x_{Co} = 100$ nm and $\pi_{Au} - \pi_{Co} = 27$ mV. For the thermal conductivity the values $\kappa_{Au} = 310\ W\ m^{-1}\ K^{-1}$ and $\kappa_{Co} = 70\ W\ m^{-1}\ K^{-1}$ have been used.

### 3.2. Onsager reciprocal relation

The ORR in the thermoelectric phenomena implies that $\pi = TS$. It is a consequence of the principle of microscopic reversibility built into the framework of a general statistical theory of irreversible processes. Although this relation is generally accepted, we would like to emphasize that it is still to be experimentally confirmed. The measurement of $\pi$ and $S$ for a single material cannot be carried out, and we can only measure $\pi_{Y} - \pi_{X}$ and $S_{Y} - S_{X}$ for a couple X/Y. Very few papers reports measurements of the Peltier coefficient and, as we have shown above, accurate measurements are difficult to obtain. We expect that the theory developed in this paper may help to provide sound values on the Peltier coefficient and, hence, provide a better basis for the experimental confirmation of the ORR.

### 3.3. Thomson's coefficient

Very few authors have developed methods for measuring this coefficient. The Fourier term also plays an important role in the corresponding energy balance, as shown in equation (8). Hoyem [5] and Ware [6] measured the Thomson coefficient in a Zn crystal. The ends of this conductor were maintained at temperatures $T^{I}$ and $T^{II}$ (see figure 1). Then they determined

two electric currents $I_p$ (positive) and $I_n$ (negative) which provide the same temperature at the middle of the system. They assumed identical Fourier's terms $\Delta[\kappa A(\mathrm{d}T/\mathrm{d}x)]_p = \Delta[\kappa A(\mathrm{d}T/\mathrm{d}x)]_n$ and identical heat fluxes $(J_Q)_p = (J_Q)_n$, and evaluated the Thomson coefficient from $I_p \int_{T^I}^{T^{II}} \tau \, \mathrm{d}T + R(I_p)^2 = I_n \int_{T^I}^{T^{II}} \tau \, \mathrm{d}T + R(I_n)^2$. But we have to be aware that very small deviations $\delta$ in a temperature gradient generate very large changes in the Thomson coefficient. In particular, using the following data from [5], $\tau = 1.4 \ \mu\mathrm{V} \ \mathrm{K}^{-1}$, $I_p = 1.0 \ \mathrm{A}$, $\Delta T = 99 \ \mathrm{K}$, $\kappa = 110 \ \mathrm{W} \ \mathrm{m}^{-1} \ \mathrm{K}^{-1}$, $A = 7.1 \ \mathrm{mm}^2$ and $x^{II} - x^I = 15 \ \mathrm{cm}$, we can estimate that $\tau$ varies more than a 50% due to a deviation $\delta = 0.03\%$ in $(\mathrm{d}T^I/\mathrm{d}x)_p$.

In the method developed by Lander [7] the system was intensively refrigerated at the two ends ($T^I \approx 300 \ \mathrm{K}$) and an electric current yielded a temperature distribution with a maximum at the middle ($440 \ \mathrm{K} < T^{II} < 2600 \ \mathrm{K}$) being $\mathrm{d}T^{II}/\mathrm{d}x = 0$. He considered radiation and convection losses to be negligible compared to the Fourier term, $J_Q \ll \kappa A(\mathrm{d}T^I/\mathrm{d}x)$. He assumed for the energy balance $-\kappa A(\mathrm{d}T^I/\mathrm{d}x) + I \int_{T^I}^{T^{II}} \tau \, \mathrm{d}T + I \Delta \psi = 0$. From the measurements of $T^I$, $T^{II}$ and $\mathrm{d}T^I/\mathrm{d}x$ the Thomson coefficient was evaluated. For calculating $\Delta \psi$ a correlation $\psi \propto T$ was deduced. Using the following data from [7], $\tau = 11 \ \mu\mathrm{V} \ \mathrm{K}^{-1}$, $I = 30 \ \mathrm{A}$, $\Delta T = 140 \ \mathrm{K}$, $\kappa = 137 \ \mathrm{W} \ \mathrm{m}^{-1} \ \mathrm{K}^{-1}$, $A = 0.031 \ \mathrm{mm}^2$ and $x^{II} - x^I = 0.3 \ \mathrm{mm}$, we can estimate how much the value in $\tau$ is modified due to a small deviation $\delta$ in $\mathrm{d}T^I/\mathrm{d}x$. For molybdenum, the Thomson coefficient varies more than 50% if $\delta = 1.1\%$. Therefore, precise measurements of the temperature gradients are required to obtain accurate values of $\tau$.

## 4. Conclusions

(i) The thermoelectric processes have been studied in the framework of the observable quantities. One of these is the electric potential $\Delta \psi$ which is measured between the terminals of probes Z connected to system X. The other is the heat flux $J_Q$ which the system laterally dissipates towards the surroundings.

(ii) A review of some selected papers which evaluate the Peltier and Thomson coefficients has shown the important weight of the Fourier term in the energy balance. For obtaining accuracy results on these coefficients, very precise measurements of the temperature gradients are needed.

(iii) The evaluation of the Peltier coefficient $\pi_Y - \pi_X$ of the couple X/Y from the measurements of the two temperature gradients $\mathrm{d}T_X/\mathrm{d}x$ and $\mathrm{d}T_Y/\mathrm{d}x$ at the junction has been suggested.

(iv) The lack of confidence in the values of the Peltier coefficient implies that the Onsager reciprocal relation still needs to be experimentally confirmed, at least in a few cases.

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