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THE PELTIER EFFECT

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Thermodynamic consideration of thermoelectricity in metals was applied to the Peltier effect, like it was done recently for the Seebeck effect. The Peltier coefficient was derived from the difference in the total energy of electrons in two metals in contact: $\Pi=\varepsilon_0 T\ln(1+T/\Theta_V)$, where ε_0 is the 'universal' sensitivity of thermocouples and Θ_V is the characteristic temperature of a particular thermocouple.

The Peltier and Seebeck coefficients derived from the new thermodynamic model were shown not to hold the Thomson relation exactly, but only in the low-temperature limit.

Keywords: *Peltier coefficient, Seebeck coefficient, thermocouple, Thomson relation*

Introduction

The Peltier effect is the heat liberation at one junction of a thermocouple and heat sorption at the other, when an electric current flows in the circuit. It was discovered in 1834, thirteen years after the Seebeck effect (1821). Both thermoelectric effects were considered of the same nature. Theory of thermoelectricity was developed by Thomson (Lord Kelvin) on the background of the charge carriers dynamics in metals, with the Thomson effect proposed ad hoc.

Quantitative relations for the Seebeck effect were derived from classical mechanics by Drude and later on from quantum physics by Sommerfeld. Theory of the Peltier effect was not developed in such a way, but the relationship between Seebeck coefficient (ε) and Peltier coefficient (Π) was derived from thermodynamic considerations by Thomson: $\Pi=\varepsilon T$ [1].

The Peltier effect is used in thermal analysis and calorimetry for calibration [2, 3] and heat flow compensation [4]. Cooling devices on the Peltier effect are used for the design of isothermal microcalorimeters [5], superconducting magnets [6] and PC processors [7]. The Peltier effect is included in theoretical and laboratory university courses as one of thermoelectric phenomena [8].

Current theory of thermoelectricity is based on the non-equilibrium approach, considering the electromotive force (*emf*) of a thermocouple the result of a gradient of the electron concentration in a metal with the temperature gradient [9–12]. According to the theory, the emf of a thermocouple is the difference in the integrals for the absolute Seebeck coefficients (S) of two constituent metals (A and B)

$$\Delta U=\int_{T_1}^{T_2}(S_A-S_B)\mathrm{d}T$$

where T_1 and T_2 are the junction temperatures. Neither ΔU nor S can be represented by a universal function of temperature, because the temperature distribution inside the arms of a thermocouple is specific for every measurement. This theoretical conclusion contradicts to the well-known fact that the emf of a thermocouple depends only on the temperatures T_1 and T_2 (the low of Magnus) [11, 13]. Application of thermocouples as a tool for the accurate temperature measurements is based, in fact, on the idea that the emf is the result of the temperature difference, not integration along the arms. Anyway, the non-equilibrium theory failed to derive the emf of a thermocouple as a function of temperature.

Recently, equilibrium thermodynamic model for the Seebeck effect was derived from the Gibbs energy of electrons in two metals in contact [14]. The model yields the emf of a thermocouple as a function of temperature, fitting the experimental values of ΔU and ε very well at low temperatures. The model was tested using the data for E, J, K, N, R, S and T type thermocouples.

The objective of this work was to develop the quantitative model for the Peltier effect, using the theory applied recently for the Seebeck effect.

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Relation between Seebeck and Peltier effects

It was shown in the new thermodynamic model [14] that the voltage at the point of a contact between two metals is

$$U(T)=\varepsilon_0\left[T-\Theta_V \ln\left(1+\frac{T}{\Theta_V}\right)\right] \tag{1}$$

where ε_0 is the limiting theoretical value of the thermocouple sensitivity, and Θ_V is the characteristic temperature of a particular thermocouple, depending on the metals. These two parameters are calculated according to equations

$$\varepsilon_0=\frac{k_B}{e}=86.17\ \mu\text{V K}^{-1} \tag{2}$$

where k_B is the Boltzmann constant and e is the elementary charge, and

$$\Theta_V=\frac{2R}{\gamma_A-\gamma_B} \tag{3}$$

where R is the gas constant, γ_A and γ_B are the coefficients of electronic heat capacity (C_e) for metals A and B in the thermocouple:

$$C_{ei}=\gamma_i T \tag{4}$$

One more relationship will be used below:

$$R=N_0 k_B \tag{5}$$

where N_0 is the Avogadro number.

Figure 1a shows two wires of metals A and B, forming the thermocouple with junctions 1 and 2. Left junction is at temperature T_1 and right one at T_2. There is a voltage of $U(T_i)$ at each junction. The value of the voltage is described by Eq. (1). Wire B is interrupted, and the voltage of

$$\Delta U=U(T_2)-U(T_1) \tag{6}$$

is at the contacts. If the circuit is closed, an electric current appears. The diagram of the circuit is shown in Fig. 1b. Here r is the equivalent load that defines the current (i) in the circuit:

$$i=\frac{\Delta U}{r} \tag{7}$$

Let us consider the changes in the energy of electrons passing through the junction. The voltage at the junction of a thermocouple was derived from the thermodynamic equilibrium of the electron systems in two metals in contact. Under equilibrium, the Gibbs functions of electrons in metals A and B are equal:

$$\Delta G=\Delta H-T\Delta S+\Delta U\Delta q=0 \tag{8}$$

where ΔH is the difference in enthalpy, ΔS is the difference in entropy, and ΔU is the voltage at the junction.

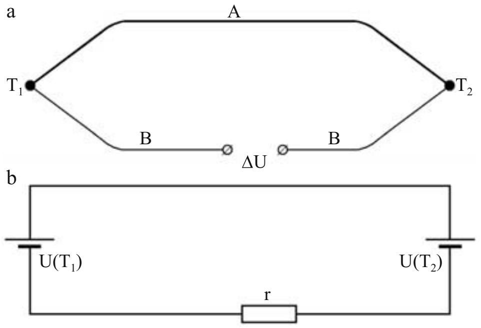

Fig. 1 a – Thermocouple made from two dissimilar metal wires (A and B) with two junctions kept at two different temperatures (T_1 and T_2). Wire B is interrupted and there is a voltage of ΔU at the contacts. b – Diagram of equivalent electric circuit for the evaluation of a current through the junctions of the thermocouple

For the sake of definiteness, let the thermal energy of electrons in metal 'A' be greater than that in metal 'B':

$$H_A=\frac{1}{2}\gamma_A T^2>H_B=\frac{1}{2}\gamma_B T^2 \tag{9}$$

Less thermal energy in metal 'B' is compensated partly by increased electrostatic energy. By convention, the potential energy of electrostatic interaction is defined against zero energy level chosen at will. To simplify the evaluations, let the electrostatic energy of electrons in metal A be equal to zero. Total energy of electrons in metal 'A' is equal to their thermal energy (enthalpy):

$$E_A=H_A=\frac{1}{2}\gamma_A T^2 \tag{10}$$

For metal 'B', this is the sum of enthalpy and electrostatic energy:

$$E_B=H_B+U\Delta q=\frac{1}{2}\gamma_B T^2+U\frac{eN}{\Theta_V}T \tag{11}$$

The term for Δq was substituted here by using two formulas:

$$\Delta q=2e\Delta N=2e\alpha T \tag{12}$$

and

$$\Theta_V=\frac{N}{2\alpha} \tag{13}$$

In Eq. (12) the assumption is used that the voltage at the junction of a thermocouple is generated only by the electrons with energy greater than the Fermi level. The number of the electrons increases linearly with temperature and is a fraction of the total amount of electrons, with coefficient α for the calculation of the fraction. Equation (13) is the definition of the characteristic temperature. Both equations were discussed in [14] as Eqs (26) and (33), respectively.

Equation (8) states that the Gibbs functions (chemical potentials) of electrons at the contact between metals 'A' and 'B' are equal under equilibrium, but their total energies are not, because the Equation contains also the entropy contribution ($T\mathrm{d}S$). This is the reason why an electron liberates or absorbs energy if passes from one metal to the other. Electrons diffuse readily through the border between the metals, and under equilibrium the number of electrons passing from 'A' to 'B' is equal to those passing from 'B' to 'A'. Net energy change is equal to zero. The equilibrium is violated if there is a flow of electrons in either direction. Electrons pass the border in one direction continuously, producing constant either lack of or excess in energy and resulting in either heating or cooling at the junction.

Difference in the total energy of two phases in contact under thermodynamic equilibrium can be illustrated by the isothermal first-order phase transition, melting or boiling [15, 16]. For the melting-freezing case, liquid and solid phases are separated by the phase boundary and this two-phase system is stable, because the chemical potentials of the phases are equal. Molecules (or atoms) can readily pass from liquid phase to solid and back, resulting in the recrystallization. Nevertheless, the total energy of molecules in the phases is different. If the amount of one phase increases and the other decreases, the net heat effect occurs. Heat is liberated for additional crystallization and absorbed for additional melting. This example is considered here for the illustration of conventional phenomenon of the net energy difference between two phases under equilibrium, with equal Gibbs energies.

Let us consider now the current in the circuit, arising after the closure of the contacts. If the temperature of the junction under consideration is greater than that of the other one, electrons in the whole circuit move in the direction defined by the electrostatic voltage at the junction considered, i.e., from metal 'B' to metal 'A'. Difference in the energy of electrons crossing the border between the metals at the junction is

$$E_{\mathrm{B}}-E_{\mathrm{A}}=\frac{1}{2}\gamma_{\mathrm{B}}T^{2}+U\frac{eN}{\Theta_{\mathrm{V}}}T-\frac{1}{2}\gamma_{\mathrm{A}}T^{2} \tag{14}$$

Let the number of electrons passing through the junction be equal to the Avogadro number ($N=N_0$). Using Eqs (1) and (2) for the voltage at the junction, we have

$$E_{\mathrm{B}}-E_{\mathrm{A}}=\frac{k_{\mathrm{B}}}{e}\frac{eN_{0}}{\Theta_{\mathrm{V}}}T\left[T-\theta_{\mathrm{V}}\ln\left(1+\frac{T}{\Theta_{\mathrm{V}}}\right)\right] -\frac{1}{2}(\gamma_{\mathrm{A}}-\gamma_{\mathrm{B}})T^{2} \tag{15}$$

Substituting the coefficients according to Eqs (3) and (5), we receive the final formula for the energy change:

$$\begin{aligned}E_{\mathrm{B}}-E_{\mathrm{A}}&=\frac{RT}{\Theta_{\mathrm{V}}}\left[T-\Theta_{\mathrm{V}}\ln\left(1+\frac{T}{\Theta_{\mathrm{V}}}\right)\right]-\frac{RT^{2}}{\Theta_{\mathrm{V}}}\\&=-RT\ln\left(1+\frac{T}{\Theta_{\mathrm{V}}}\right)\end{aligned} \tag{16}$$

The change in the total energy of electrons is opposite in sign to the change in their electrostatic energy. If charged particle moves freely in electric field, the energy is liberated. The opposite sign means that the energy is absorbed at the hot junction of a thermocouple. The hot junction is cooled, and the cold one is heated.

Thus, the difference in temperature between two junctions of a thermocouple results in the voltage, if the circuit is interrupted. The voltage depends on temperature, with functional relation expressed by Eq. (1). This is the Seebeck effect. If the circuit is closed, the electric current heats up the cold junction and cools down the hot one. This effect of the current decreases the difference in temperature between the junctions of the thermocouple. If an external power supply is switched into the circuit, it generates an electric current, cooling down one junction and heating up the other, depending on the direction of the current. This is the Peltier effect.

The Peltier coefficient

The rate of liberation or absorption of the heat at the junction of a thermocouple is proportional to the magnitude of a current, i,

$$\frac{\mathrm{d}Q}{\mathrm{d}t}=\Pi i \tag{17}$$

where Π is the Peltier coefficient by definition [1]. The current, in turn, is the rate of a charge flow through the circuit:

$$i=\frac{\mathrm{d}q}{\mathrm{d}t} \tag{18}$$

Equation (17) can be integrated with respect to the time. Portion of heat, released or absorbed, is proportional to the electric charge passed through the junction of a thermocouple:

$$\Delta Q=\Pi\Delta q \tag{19}$$

Our thermodynamic model for the Seebeck effect yields Eq. (16) for the relation between the energy difference in the electronic system with the charge of eN_0 passed through the junction. The Peltier coefficient can be calculated as follows:

$$\Pi=\frac{\Delta Q}{\Delta q}=\frac{E_{\mathrm{B}}-E_{\mathrm{A}}}{eN_0}=-\frac{R}{eN_0}T\ln\left(1+\frac{T}{\Theta_{\mathrm{V}}}\right)$$
$$=-\varepsilon_0 T\ln\left(1+\frac{T}{\Theta_{\mathrm{V}}}\right) \quad (20)$$

It is interesting to compare this explicit equation for the Peltier coefficient with the equation derived from the Thomson relation for the Peltier and Seebeck coefficients:

$$\Pi(T)=T\varepsilon(T) \quad (21)$$

As the Seebeck coefficient in our model is

$$\varepsilon(T)=\varepsilon_0\frac{T}{\Theta_{\mathrm{V}}+T} \quad (22)$$

we have

$$T\varepsilon(T)=\varepsilon_0\frac{T^2}{\Theta_{\mathrm{V}}+T} \quad (23)$$

Equations (20) and (23) for the Peltier coefficients differ evidently from one another. Thus, the Thomson relation does not hold strictly for our thermodynamic model. The situation is very interesting. The Thomson relation was derived from thermodynamic considerations in 1854. At that time, thermodynamics was not developed in its complete form yet. The Gibbs potential, thermodynamic equilibrium, the phase rule, etc., were not known at the time. Entropy was the only instrument for thermodynamic analysis. The considerations of Thomson were very simple and based on the analogy with gas laws. Hypothetical electrical liquid (electron was also unknown at the time) was considered to evaporate at one junction of a thermocouple and to condense at the other, with its particular ‘heat capacity’ as the mechanism for the heat transfer by the electricity between the junctions. On the other hand, our model was also derived from thermodynamic considerations. But now the electrons (electric charge carriers), chemical potential (normalized Gibbs energy) and thermodynamic equilibrium are involved. The new model has two simplifications: (1) the number of electrons generating the voltage at the junction is very small as compared with the total number of electrons in the metals and (2) the temperature is very small as compared with the characteristic parameter Θ_{V}. Let us check the Thomson relation for the low-temperature limit, where $T \ll \Theta_{\mathrm{V}}$. Equations (20) and (23) transform into two new equations:

$$\varepsilon_0 T\ln\left(1+\frac{T}{\Theta_{\mathrm{V}}}\right)\approx\varepsilon_0\frac{T^2}{\Theta_{\mathrm{V}}} \quad (24)$$

$$\varepsilon_0\frac{T^2}{\Theta_{\mathrm{V}}+T}\approx\varepsilon_0\frac{T^2}{\Theta_{\mathrm{V}}} \quad (25)$$

Thus, the Thomson relation for the Seebeck and Peltier coefficients is valid in the low-temperature limit.

We cannot test Eq. (20) against experimental values for the Peltier coefficients right now, like it was done for the Seebeck coefficient and the emf for letter-designed thermocouples [14], because accurate data on the Peltier coefficients are missing in the literature. To measure the Peltier coefficient is much more difficult than the Seebeck coefficient [17]. The accuracy of the Peltier coefficient measurements was not high enough even to test the Thomson relation [18], when the thermocouples were successfully used for the accurate measurements of temperature [19]. Accurate measurements of the Peltier coefficient are planned in our future work.

Conclusions

The Peltier and Seebeck effects are shown to be closely related within the new thermodynamic model applied recently to the quantitative theory of the Seebeck coefficient. In this work, the model was developed for the evaluation of the Peltier coefficient. It is shown to be a function of temperature and characteristic parameter Θ_{V}, like the Seebeck coefficient. The Thomson relation does not hold strictly for the two coefficients, but is valid in the low-temperature limit.

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