Review of: "Thermopower of ionic conductors and ionic capacitors"

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Comments on “Thermopower of ionic conductors and ionic capacitors” by A. Würger (Phys. Rev. Res. 2, 042030(R), 2020)

In this paper, we give some comments on the paper published by Wurger (Phys. Rev. Res. 2, 042030(R), 2020)[1]. Firstly, we discuss the thermoelectric effect in general, referring to the discussion performed in analysed Wurger’s paper [1]. We show a detailed physical sense of the effective Peltier coefficient formula derived therein. We also show that a similar formula for the Seebeck coefficient can be written instantly. Then, we focus on the derivation of Eqs. (18) and (19) in [1] and unexpected conclusions, that can be drawn from this analysis. Finally, we propose another method of deriving the formula for the effective Seebeck coefficient. In our opinion, the use of this formula is clearer and substantively correct.

1. Heat of transport and transported heat

In the paper reported by Wurger et al.[1], the author defines the Seebeck coefficient (in this paper we will use α instead of *S* like in [1]) as “heat of transport” (in this paper:Q^* instead of *Q*, like in [1]) divided by temperature (*T*) and charge of a considered carrier (*q*):

$$\alpha = \frac{Q^*}{qT} \qquad (1.1)$$

Using the definition of entropy, the Seebeck coefficient becomes “entropy of transport”S^* divided by the electrical charge *q*, and this is presented by Eq. (1.2):

$$\alpha = \frac{S^*}{q} \qquad (1.2)$$

However, from Callen’s derivation of the thermoelectric effect based on Onsager equations[2], it follows, that the Seebeck coefficient is “entropy transported by the flowing carrier” divided by the charge of this carrier [3]. Following [4], the Seebeck coefficient consists of the presence part and the transport part, and the “heat of transport” is related to the second part. This may be expressed as:

$$\alpha = \frac{S}{q} + \frac{Q^*}{qT} \qquad (2)$$

The first part of Eq. (2) is related to the entropy per particle itself, disregarding effects occurring during the transfer from one position to another. However, this can be considered as a matter of nomenclature, as long as Q/qT in the discussed paper states the Seebeck coefficient of a given carrier (both present and transport part).

2. Kelvin (or Thomson) relations

In Eq. (6) in paper [1], the author seems to be applying the definition of Peltier coefficients given by Callen et al. in[2] (see eq. (30) in [2]). Summarizing flows of two charge carrier types and inserting fundamental Ohm’s law for current density we obtain:

$$\dot{q} = \pi \boldsymbol{J} = \pi_1 \boldsymbol{J}_1 + \pi_2 \boldsymbol{J}_2 = \pi_1 \sigma_1 \boldsymbol{E} + \pi_2 \sigma_2 \boldsymbol{E} = \left(t_1 \pi_1 + t_2 \pi_2\right) \sigma \boldsymbol{E} = \left(t_1 \pi_1 + t_2 \pi_2\right) \boldsymbol{J} \qquad (3)$$

where t_i denotes a transference number of i - charge carrier and π is a Peltier coefficient, $\dot{q}$ is a rate of heat flow and $\boldsymbol{E}$ denotes an electrical field intensity. In a similar manner, Eq. (8) in [1] can be derived from Eq. (43) in Callen’s paper. The Kelvin relations, including

$$\pi = \alpha T \qquad (4)$$

have been obtained by Callen et al.[2] from the abovementioned equations (eq. (50) in[2]). In our opinion, obtaining the same results from the same definitions cannot be considered as ‘verification’. Therefore, in our opinion, such considerations presented in the publication [1] are incorrect from a scientific point of view.

3. Electrical and electrochemical potential

It is worth underlining, that in the case of Onsager equations used to describe the thermoelectric effect (see Eq. (18) in [2]), the “thermodynamic force” (denoted as X in this work) causing a flow of particles is a gradient of electrochemical potential $\nabla\tilde{\mu}$ divided by temperature T. This may presented as Eq. (5):

$$X_1 = T^{-1} \nabla \tilde{\mu} = T^{-1} \nabla (\mu + q\varphi) \qquad (5)$$

This expresses, that the flow of mobile carriers results from the gradient of both electrical potential φ (Ohm’s law) and chemical potential μ (Fick's law). However, the author of [1] describes the current (flow of charged particles) using only a part related to Ohm's law: **J**=σ**E**, (see *e.g.* Eq. (4) in [1]). Moreover, in [1], a vector of electrical field intensity **E** is also used in Gauss law (see Eq. (12) in [1]), where it definitely refers to the electrical potential gradient. In our opinion, this approach is totally inconsistent with the general thermodynamic description of the thermoelectric effect. Notice also, that this difference of electrochemical potential of electrons is available for measurement *i.a.* by using a voltmeter (see a theoretical paper reported by Riess [5]).

4. Adding thermoelectric effects with transference numbers weights – Peltier effect

Wurger [1] considers the Peltier effect in a system without a temperature gradient (see Fig. 1c in[1]). As can be seen, there is no thermoelectric voltage (since there is no temperature gradient) and there is no chemical potential difference, due to the constant concentration of mobile ions. The electrical current flows only due to the external electric field, following Ohm's law $\boldsymbol{J}=\sigma\boldsymbol{E}$. For each carrier type, $\boldsymbol{J_i}=\sigma_i\boldsymbol{E_i}$ (*i* stands for carrier type) is fulfilled. This situation is described by Eq. (3) herein and Eq. (6) in [1]. This derivation shows the reasonableness of the effective Peltier coefficient formula:

$$\pi = \sum t_i \pi_i \qquad (6)$$

5. Nature of thermoelectric coefficients and Thomson relations

The thermoelectric phenomenon is a conjugation of carriers' transport (electrical current) and heat flow[3]. Considering the Onsager equation for these two flows [2], one can notice, that the conjugation of the two fluxes (related to charged particles and heat flow) is proportional to the L_{12} element of the kinetic parameters matrix. These parameters are characteristics that are features of the carriers in the system, not parameters of external conditions (gradients, flows).

Different "types" of thermoelectric effects can be observed in different conditions, e.g.

- pure Peltier effect is observed in a system with flows induced only by the external electrical field (as discussed above);
- the Seebeck effect is observed in an open circuit system with a temperature gradient.

The respective coefficients (Peltier and Seebeck) can be obtained by solving the Onsager equation for appropriate conditions and these coefficients are functions of the kinetic parameters, not the applied conditions. Comparing these functions, Thomson relations can be obtained. Therefore, we conclude, that the Seebeck coefficient (of a given conducting medium) is the same in all conditions and the Thomson relation, represented by Eq. (4), can be applied. Inserting Eq. (6) to Eq. (4), the effective Seebeck coefficient can be obtained and presented by Eq. (7):

$$\alpha = \frac{\pi}{T} = \frac{1}{T} \sum t_i \pi_i = \sum t_i \alpha_i \qquad (7)$$

6. Errors in Würger's approach and an unexpected conclusion from his equations

In our opinion, in Eq. (10) in paper[1], a wrong definition of the Seebeck coefficient is used. The Seebeck coefficient relates the temperature gradient with the gradient of electrochemical potential, not the gradient of electrical potential. Thus, we believe that it makes the further derivation of Eqs. (18) and (19) in [1] is incorrect. For example, we can consider a system with one type of mobile carrier, compensated by an immobile structure (e.g. solid state ionic conductor). Such a system can be considered as a system with two types of carriers (which can have a similar concentration). One of these carriers has mobility equal to zero. Thus, no transport effects can be related to particles of this kind, and the thermoelectric effect will not be observed. However, according to Eqs. (18) and (19) in [1], this rigid, immobile structure contributes to the thermoelectric effect. We think, that such an analysis seems to make no physical sense and should be corrected.

7. Alternative derivation of the effective Seebeck coefficient

In order to determine the effective Seebeck coefficient, we can consider a mixed–conducting material with two types of carriers (named charge 1 and charge 2) which can be electrons of ions. Then, let's represent the transport parameters of these carriers by parallel resistors R_1 and R_2, where R_1 and R_2 correspond to the charge carrier 1 and 2, respectively. The schemes of electrochemical equivalent circuits related to the transport of these carriers are shown in Fig. 1. In separate branches (situation shown in Fig.1a), under a temperature difference ΔT, the different electrochemical potential of electrons will be generated as a result of the thermoelectric effect (provided, that electrodes, reversible for electrons and respective carriers, are present at both sides of the material). This generation of electrochemical potential difference can be described by voltage sources U_1 and U_2.

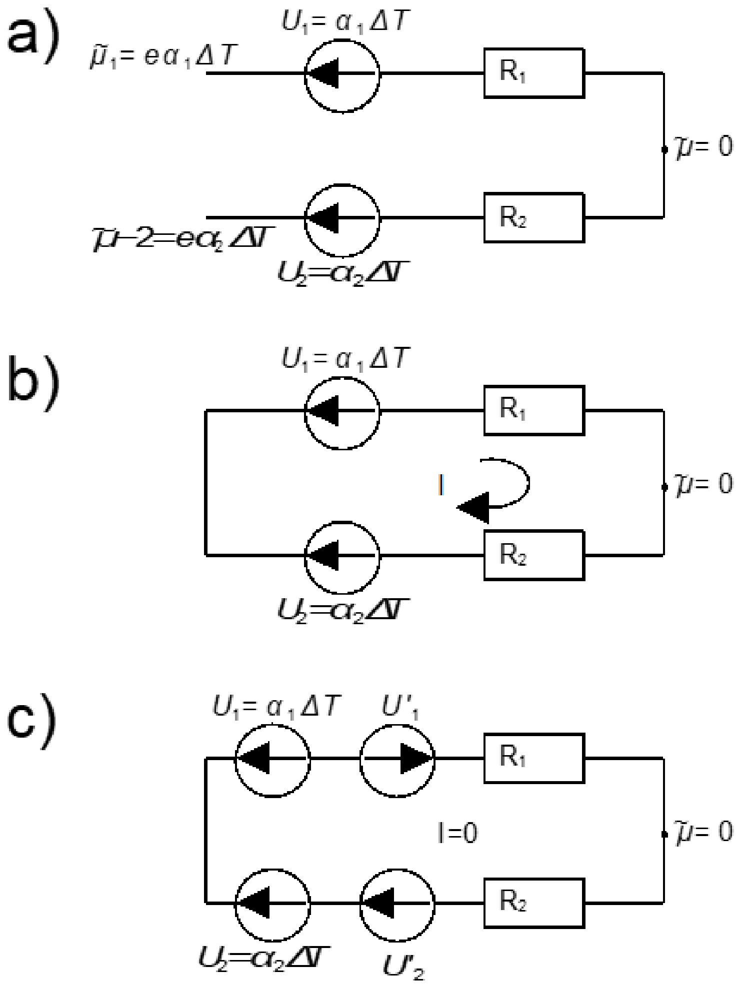

Fig.1. *Scheme of electrochemical equivalent circuits for theoretical determination of an effective Seebeck coefficient.*

However, in the material with mixed conduction, the two branches are shorted on both sides. When circuit (a) is closed (situation shown in Fig.1b), the circuit is under a non-steady state condition, since different potentials are shorted. This results in a flow of initial electrical current I:

$$I = \frac{\left(\alpha_1 - \alpha_2\right)\Delta T}{R_1 + R_2} \qquad (8)$$

where α_1 and α_2 denote a Seebeck coefficient of carriers 1 and 2, respectively. In the initial state (t→ 0), the voltage drops at the resistors equal to IR_1 and IR_2 will compensate voltage difference between branches.

The flowing electrical current will result in a change of potentials on the left-hand side of the circuit, which are represented by additional sources U'_1 and U'_2. In a finally reached steady-state, the voltages U'_1 and U'_2 will completely compensate the difference between U_1 and U_2 so that no electrical current flows (see the situation in Fig.1c). The steady-state voltage V_f is then observed and can be expressed as:

$$V_f = \alpha_1 \Delta T - U_1' = \alpha_2 \Delta T + U_2' \qquad (9)$$

It can be noticed, that in the initial state, the difference between U_1 and U_2 is only compensated by voltage drops at resistors (IR_1 and IR_2) and in the steady state by U'_1 and U'_2. Therefore, we can see that:

$$U_1' = IR_1 \qquad (9.1)$$

$$U_2' = IR_2 \qquad (9.2)$$

The final steady state voltage V_f can be obtained by inserting Eq. (9.1) and Eq. (8) into Eq. (9):

$$V_f = \alpha_1 \Delta T - U_1' = \alpha_1 \Delta T - \frac{R_1}{R_1 + R_2}\left(\alpha_1 - \alpha_2\right)\Delta T = \left(\frac{R_2 \alpha_1}{R_1 + R_2} + \frac{R_1 \alpha_2}{R_1 + R_2}\right)\Delta T$$

$$= \left(\frac{\sigma_1 \alpha_1}{\sigma_1 + \sigma_2} + \frac{\sigma_2 \alpha_2}{\sigma_1 + \sigma_2}\right)\Delta T = \left(t_1 \alpha_1 + t_2 \alpha_2\right)\Delta T \qquad (10)$$

Where σ_1 and σ_2 denote electrical conductivities of charge carriers 1 and 2, respectively. Therefore we can see, that the effective Seebeck coefficient is obtained only by taking partial Seebeck coefficients and transference numbers of the carriers.

$$\alpha = (t_1 \alpha_1 + t_2 \alpha_2) \qquad (11)$$

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