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**UNIVERSAL NONEQUILIBRIUM THERMODYNAMICS
AND THE SEEBECK EFFECT**

In conformity with a book by I. Prigogine and D. Kondepudi “Modern Thermodynamics”, this paper describes the Seebeck effect based on Onsager’s linear thermodynamics, on the a priori assumption that only a generalized heat flow is different from zero. Moreover, in such situations it is considered that a thermodynamic system is in close to equilibrium state (linear mode). It is proposed to consider the above effect in the framework of universal nonequilibrium thermodynamics, where it is shown that the importance of the Seebeck effect lies in confirming the validity of Onsager’s reciprocity relations, since the necessity of making any assumptions as to proximity to equilibrium state is eliminated. The effect is shown to be an illustrative example confirming the adequacy of universal nonequilibrium thermodynamics. Next, a thermodynamically-phenomenological description of the Seebeck effect based on the proposed universal nonequilibrium thermodynamics is provided. The results testify that the Seebeck effect, without experiments, proves not only the validity of Onsager’s reciprocity relations, but also the absurdity of Onsager’s thermodynamics and of the Prigogine principle of minimum entropy production. Onsager’s thermodynamics is absurd because being thermodynamics of reversible processes is called thermodynamics of irreversible processes. And the Prigogine principle is absurd because minimum entropy production being equal to zero is considered to be more than zero.

Key words: universal nonequilibrium thermodynamics, reversibility, irreversibility, Onsager’s thermodynamics, Prigogine principle, Seebeck effect, Onsager’s reciprocity relations, entropy production, perpetual motion machine, steady-state process, the second law of thermodynamics, scientific revolution.

Introduction

To illustrate the applications of Onsager’s reciprocity relations, I. Prigogine and D. Kondepudi in their book “Modern Thermodynamics” consider in detail the thermoelectric effects, specifically, the Seebeck effect [1].

As the first illustration, they consider the thermoelectric effects whereby there is heat flow \overline{J}_q and electric current \overline{J}_e in conductors (subscript e means that this refers to electron flow). In this case, entropy production in the unit volume and the related linear phenomenological laws are written as follows [1]:

$$\sigma = \overline{J}_q \cdot \nabla \left(\frac{1}{T} \right) + \overline{J}_e \cdot \frac{\overline{E}}{T} \quad (1)$$

$$\vec{J}_q = L_{qq} \nabla \left(\frac{1}{T} \right) + L_{qe} \frac{\vec{E}}{T}, \quad (2)$$

$$\vec{J}_e = L_{ee} \frac{\vec{E}}{T} + L_{eq} \nabla \frac{1}{T}, \quad (3)$$

where \vec{E} is electric field. For the one-dimensional system, such as conductors, the vector character of \vec{J}_q and \vec{J}_e is of no importance, and the two flows can be regarded as scalars. In order to relate coefficients L_{qq} and L_{ee} to thermal conductivity K and resistance R , one can write equations (2) and (3) in the one-dimensional system as

$$J_q = -\frac{1}{T^2} L_{qq} \frac{\partial T}{\partial x} + L_{qe} \frac{E}{T}, \quad (4)$$

$$J_e = L_{ee} \frac{E}{T} - \frac{1}{T^2} L_{eq} \frac{\partial T}{\partial x}. \quad (5)$$

The Fourier law of thermal conductivity is valid in the absence of electric field, i.e. $E = 0$. Comparison of expression for thermal conductivity

$$J_q = -\left(\frac{1}{T^2} \right) L_{qq} \frac{\partial T}{\partial x} \quad (6)$$

to the Fourier law $J_q = -K \frac{\partial T}{\partial x}$ (7)

leads to the relation

$$K = \frac{L_{qq}}{T^2}. \quad (8)$$

To find the correlation between L_{ee} and resistance R , note that electromotive force (EMF) is expressed by the following formula

$$V = -\nabla \phi = \int_0^l E dx \quad \text{or} \quad J_e l = \frac{L_{ee}}{T} V. \quad (9)$$

Comparison of this equation to Ohm's law

$$J_e = \frac{V}{R} \quad (10)$$

yields $L_{ee} = T \frac{l}{R} = \frac{T}{r}$, (11)

where r is resistance per unit length. As long as Ohm's law can be formulated in general form as

$$\vec{J}_e = \frac{\vec{E}}{\rho}, \quad (12)$$

where ρ is resistivity, comparing (5) on condition of $\frac{\partial T}{\partial x} = 0$ to (12), we get

$$L_{ee} = \frac{T}{\rho}. \quad (13)$$

In the one-dimensional system ρ is substituted by r , i.e. resistance per unit length.

In the above formulae, cross coefficients L_{qe} and L_{eq} can be also related to the experimentally measured values.

For instance, in the Seebeck effect, the temperature difference between two contacts of different metallic conductors generates EMF. This EMF is measured at the zero current, i.e. at $J_e = 0$. For such a system one can use equations (4) and (5). In (5), assuming that $J_e = 0$, we get

$$0 = L_{ee}ET - L_{eq} \frac{\partial T}{\partial x}. \quad (14)$$

To derive a relationship between the temperature difference ΔT of contacts and the EMF generated by this temperature difference, $\Delta\phi = -\int Edx$, let us integrate this equation. In so doing, we suppose that full change in ΔT is small, and one can use the approximation

$$\int TE dx \approx T \int E dx = -T\Delta\phi. \quad (15)$$

Then

$$L_{eq} = -L_{ee}T \left(\frac{\Delta\phi}{\Delta T} \right)_{J_e=0} \quad (16)$$

The experimentally measured parameter $-(\Delta\phi/\Delta T)_{J_e=0}$, is called thermoelectric power. Using (16), coefficient L_{eq} can be related to the measured values, namely coefficient L_{ee} , temperature T and thermoelectric power $-\Delta\phi/\Delta T$.

It is noteworthy that formula (16) is meaningful when thermoelectric effects are studied in close to equilibrium states and a linear mode. It means that coefficients L_{qq} , L_{ee} etc. can be regarded as constants. Since $T(x)$ is a function of coordinate x , such an assumption is, strictly speaking, is not correct. Therefore, formula (16) has a meaning not only at $J_e = 0$, but also at $\partial T/\partial x \rightarrow 0$ [1, 2].

Description of the Seebeck effect in the framework of universal nonequilibrium thermodynamics

Thus, the aforesaid testifies that the Seebeck effect, on top of everything else, is important for the experimental verification of the validity of Onsager's reciprocity relation [3], at least in close to equilibrium state.

In fact, in the framework of our universal nonequilibrium thermodynamics the importance of the Seebeck effect becomes overwhelmingly greater in confirming the validity of Onsager's reciprocity relation, since the necessity of making any assumptions as to closeness to equilibrium state is eliminated. Moreover, the Seebeck effect is one of the illustrative examples confirming the adequacy of our universal nonequilibrium thermodynamics [4].

Now, to provide proofs for our laudatory comments on the Seebeck effect, we will interpret this effect in terms of universal nonequilibrium thermodynamics. In other words, we will propose a fundamentally new thermodynamic-phenomenological description of the Seebeck effect based on the laws of universal nonequilibrium thermodynamics [5].

For compactness of writing, we introduce the following notations:

$$X_1 = -\frac{1}{T^2} \frac{\partial T}{\partial x}, \quad X_2 = \frac{E}{T}. \quad (17)$$

Then equations (1) – (3) for the one-dimensional case will take on the form:

$$\sigma = J_q X_1 + J_e X_2, \quad (18)$$

$$J_q = L_{qq} X_1 + L_{qe} X_2, \quad (19)$$

$$J_e = L_{eq} X_1 + L_{ee} X_2. \quad (20)$$

In this case, J_q and J_e are called generalized flows, and X_1 and X_2 – generalized forces.

According to the second law, with regard to (19) and (20), relation (18) will take on the form

$$\sigma = L_{qq} X_1^2 + (L_{qe} + L_{eq}) X_1 X_2 + L_{ee} X_2^2 \geq 0 \quad (21)$$

that is, in the nonequilibrium state of thermodynamic system the local values of entropy production (σ) are not negative. Within the framework of the Onsager thermodynamics and in the book by I. Prigogine and D. Kondepudi “Modern Thermodynamics” relation (21) was replaced by the following relation [1, 3]

$$\sigma = L_{qq} X_1^2 + (L_{qe} + L_{eq}) X_1 X_2 + L_{ee} X_2^2 > 0 \quad (22)$$

with imposing the condition

$$L_{qq} > 0, L_{ee} > 0 \text{ and } (L_{qe} + L_{eq})^2 < 4L_{qq} L_{ee} \quad (23)$$

hence, a priori, the possibility of vanishing entropy production (22) under nonequilibrium states of thermodynamic systems was eliminated once and forever, and the feasibility of a perpetual motion machine of the second kind was banned [4]. The seat of the trouble is that nobody else has managed to interpret mathematically and physically adequately the second law of thermodynamics, that is, the equality sign in formula (21) has been referred only to equilibrium state of thermodynamic system, whereby the second law of thermodynamics was from the outset placed on the Procrustean bed of irreversible thermodynamics based on relations (22) and (23) [6].

In fact, according to universal nonequilibrium thermodynamics, for relation (21) to be valid, it is necessary and sufficient to impose on it the following conditions [4]:

$$L_{qq} > 0, L_{ee} > 0 \text{ and } (L_{qe} + L_{eq})^2 - 4L_{qq} L_{ee} = 0. \quad (24)$$

Thus, relation (21) with conditions (24) is an adequate mathematical model of the second law of thermodynamics as applied to the description of nonequilibrium irreversible and reversible states of thermodynamic systems with two generalized flows, and here the coefficients of equations (19) and (20) L_{qq} , L_{qe} , L_{eq} , L_{ee} can be the functions of intensive parameters of thermodynamic system. Such situation testifies that in the framework of universal nonequilibrium thermodynamics the linear reversible and linear irreversible thermodynamics, as well as the nonlinear reversible and nonlinear irreversible thermodynamics are partial cases of universal nonequilibrium thermodynamics [4]. Therefore, it appears that reversibility, just as irreversibility, is the inseparable attribute of real nonequilibrium processes, in other words, all steady-state nonequilibrium processes of transfer in thermodynamic systems with two and more generalized flows are reversible due to the fact that in such situations the local values of entropy production in thermodynamic system are equal to zero.

Since in the Seebeck effect the processes of current and heat transfer are steady-state, the nonequilibrium process is reversible because of vanishing local values of entropy production (σ), i.e.

$$\sigma = J_q X_1 + J_e X_2 = 0 \quad (25)$$

or with regard to (19) and (20):

$$\sigma = L_{qq} X_1^2 + (L_{qe} + L_{eq}) X_1 X_2 + L_{ee} X_2^2 = 0 \quad (26)$$

under conditions

$$L_{qq} > 0, L_{ee} > 0 \quad u \quad (L_{qe} + L_{eq})^2 - 4L_{qq}L_{ee} = 0 \quad (27)$$

or relations (27) can be represented as

$$L_{qe} + L_{eq} = \pm 2\sqrt{L_{qq}L_{ee}}. \quad (28)$$

Subsequent analysis showed that in (28) the negative sign before the root must be ignored, and then we have [7]:

$$L_{qe} + L_{eq} = 2\sqrt{L_{qq}L_{ee}}. \quad (29)$$

With regard to (29), relation (26) will take on the form

$$\sigma = (X_1\sqrt{L_{qq}} + X_2\sqrt{L_{ee}})^2 = 0. \quad (30)$$

From (30) it follows that:

$$X_1\sqrt{L_{qq}} + X_2\sqrt{L_{ee}} = 0. \quad (31)$$

With regard to (31), equations (19) and (20) will take on the form

$$J_q = \frac{1}{2}[L_{qe} - L_{eq}]X_2, \quad (32)$$

$$J_e = -\frac{1}{2}[L_{qe} - L_{eq}]X_1. \quad (33)$$

In so doing, if Onsager's reciprocity relation is fulfilled:

$$L_{qe} = L_{eq}, \quad (34)$$

then thermal flow J_q and electric current J_e go to zero and vice versa. Moreover, according to relations (32) and (33), even if only electric current flow vanishes, i.e. under condition $J_e = 0$, Onsager's reciprocity relation (34) is fulfilled and thermal flow J_q goes to zero.

Thus, fulfillment of traditional condition (14) in the Seebeck effect [1] is the implicit proof of the validity of famous Onsager's reciprocity relations. In its turn, the validity of Onsager's reciprocity relation (34), according to relations (32) and (33), as well as due to the second law of thermodynamics (21), clearly proves the absurdity of Onsager's thermodynamics, since in Onsager's thermodynamics not only local values of entropy production are equal to zero, but due to Onsager's reciprocity relation (34), according to relations (32) and (33), the flows J_q and J_e are also equal to zero.

Thus, the above-stated fundamental theoretical analysis of the Seebeck effect on the basis of its conceptually new thermodynamic-phenomenological description in the framework of our universal nonequilibrium thermodynamics testifies that the Seebeck effect not only proves the validity, without experiments, of famous Onsager's reciprocity relations, but also clearly proves the absurdity of Onsager's thermodynamics and Prigogine's principle of minimum entropy production.

Onsager's thermodynamics is absurd because due to Onsager's reciprocity relations, being thermodynamics of reversible processes, it is called thermodynamics of irreversible processes. Also, Prigogine's minimum entropy production principle is absurd, because minimum entropy production, being equal to zero under steady-state processes, is considered to be more than zero [8, 9].

Summary

The meaning of this paper testifies that thermodynamic scientists, since the time of formulation of the second law of thermodynamics by William Thomson and Rudolf Clausius have followed the wrong path in the development of nonequilibrium thermodynamics science due to inability to interpret adequately the second law of thermodynamics. This is also evidenced by Prigogine's statement in his Nobel Prize lecture "Even one hundred and fifty years after its formulation, the second law of thermodynamics still seems to be a program, rather than a well-developed theory in the usual sense, since nothing precise (except for the sign) is said on entropy production. Even the scope of validity of this inequality remains uncertain".

Summing up, we can say that our universal nonequilibrium thermodynamics and the Seebeck effect, complementing and enriching each other, open a new prospect for the development of nonequilibrium thermodynamics on the basis of adequate interpretation of the second law, more than a century and a half after it was formulated. As regards classical linear thermodynamics of irreversible processes, or, otherwise called Onsager's linear irreversible thermodynamics, it was just a linear thermodynamics of reversible nonequilibrium processes with the zero generalized flows. Thus, it turns out that due to famous Onsager's reciprocity relations, mankind does not possess even a linear thermodynamics of irreversible processes, to say nothing of a linear irreversible thermodynamics. Figuratively speaking, progress of thermodynamic science in the field of nonequilibrium thermodynamics has hindered for more than a century and a half due to the use of incorrect interpretations of the second law of thermodynamics and Onsager's reciprocity relations. Finally, our revolutionary new scientific achievements have made it really possible for the first time to determine correctly and unambiguously the concept of reversibility on the basis of adequate interpretation of the second law of thermodynamics. Namely, nonequilibrium process in thermodynamic system is called reversible, if local values of entropy production in the system are equal to zero, otherwise the process is called irreversible. The class of thermodynamic systems with the zero entropy production includes all thermodynamic systems that are in steady-state nonequilibrium state, therefore, all steady-state nonequilibrium processes are reversible, and the rest of nonequilibrium processes are irreversible. Against the background of these determinations of the reversible and irreversible processes, any engine that works in steady-state mode is perpetual motion machine of the second kind, inasmuch as in such a mode the local values of entropy production in the engine are equal to zero. In this connection, the existing ban on the perpetual motion machine of the second kind is once and forever withdrawn from the agenda, that is, from now on the ban on perpetual motion machine of the second kind in the framework of universal nonequilibrium thermodynamics is out of the question [10].

Thus, our universal nonequilibrium thermodynamics is a scientific revolution non only in nonequilibrium thermodynamics, but also in the historically established world outlook [4, 5].

In view of the aforesaid, from now on using classical linear nonequilibrium thermodynamics based on Onsager's reciprocity relations for solving various theoretical and practical problems from thermodynamics of irreversible processes is out of the question.

Conclusions

1. Traditional quantitative description of the Seebeck effect in the framework of Onsager's thermodynamics is incorrect for high values of transport potential gradients.
2. As a rule, the Seebeck effect is important for the experimental confirmation of the validity of Onsager's reciprocity relations only close to equilibrium.

3. In the framework of universal thermodynamics the Seebeck effect proves the validity of Onsager's reciprocity relations without imposing any restrictions on the values of transport potential gradients.
4. In the framework of universal thermodynamics all steady-state nonequilibrium processes are reversible, and all the rest of nonequilibrium processes are irreversible.
5. Any engine working in steady-state mode is a perpetual motion machine of the second kind, inasmuch as in this mode the local values of entropy production in the engine are equal to zero. In the framework of universal thermodynamics the ban on the perpetual motion machine of the second kind is inadmissible.

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