

temperature gradient $-\nabla T$ and the entropy flow density \mathbf{J}_s are conjugate and so are the negative electrochemical potential gradient $-\nabla\bar{\mu}$ and the particle flow density \mathbf{J}_e . In the two linear relations between conjugate flows and forces we can therefore set the two interaction coefficients L_{ee} and L_{se} equal to each other, in accordance with the Onsager reciprocity relation. Thus we arrive at the important phenomenological equations

$$\mathbf{J}_e = -L_{ee}\nabla\bar{\mu} - L_{es}\nabla T, \quad (3)$$

$$\mathbf{J}_s = -L_{es}\nabla\bar{\mu} - L_{ss}\nabla T. \quad (4)$$

These equations, given by de Groot, form the basis of our whole treatment of thermoelectricity, including what we shall later call the nonisothermal Volta effect. We shall see that these equations lead to a parameter called the "transport entropy per particle" which plays a role in thermodynamics comparable to that of the ordinary "static" entropy per particle in thermostatics.⁹ We have mentioned that it is often convenient to transform relations such as (3) and (4) so as to use other flows and forces, and that this transformation may lead to other physically definable and useful parameters. Therefore we shall next transform the phenomenological equations (3) and (4) into equations relating particle flow \mathbf{J}_e and a "heat flow" \mathbf{J}_q with their appropriate conjugate forces; for clarification the flow \mathbf{J}_q will be defined in terms of the flows \mathbf{J}_e and \mathbf{J}_s in such a way as to relate these to the particular flows used by Callen.¹

Following Callen, we introduce a heat current \mathbf{Q} as the difference between the total energy current \mathbf{W} and the electrochemical potential energy current $\bar{\mu}\mathbf{J}_e$:

$$\mathbf{Q} \equiv \mathbf{W} - \bar{\mu}\mathbf{J}_e. \quad (5)$$

If we associate our entropy current \mathbf{J}_s with Callen's heat current \mathbf{Q} in the manner $\mathbf{Q} = T\mathbf{J}_s$, we can write (5) in the form

$$T\mathbf{J}_s = \mathbf{W} - \bar{\mu}\mathbf{J}_e. \quad (6)$$

Separating the electrochemical potential $\bar{\mu}$ into a chemical part μ and an electrical part $-e\phi$ for electrons we have

$$T\mathbf{J}_s = (\mathbf{W} + e\phi\mathbf{J}_e) - \mu\mathbf{J}_e \equiv \mathbf{J}_q - \mu\mathbf{J}_e, \quad (7)$$

where we have combined the two terms in parentheses into a term \mathbf{J}_q which de Groot also calls a "heat current." We have therefore

$$\mathbf{J}_q = \mu\mathbf{J}_e + T\mathbf{J}_s. \quad (8)$$

Our problem now is to transform the phenomenological equations (3) and (4) from the currents \mathbf{J}_e and \mathbf{J}_s to the new currents \mathbf{J}_e and \mathbf{J}_q .

The thermodynamic theory shows that the instantaneous time rate of entropy production in an irreversible

process is given by the sum of products of conjugate currents and forces. This rate of entropy production cannot depend on the particular choice of conjugate currents and forces used to describe the process; it follows therefore that this sum is an invariant. This, then, is the condition on the transformation which is laid down by the theory. In the case of steady-state processes the sum is not only invariant but constant in time. We write this invariance for our problem in the form

$$-\mathbf{J}_e \cdot \nabla\bar{\mu} - \mathbf{J}_s \cdot \nabla T \equiv \mathbf{J}_e \cdot \mathbf{X}_e + \mathbf{J}_q \cdot \mathbf{X}_q, \quad (9)$$

each term consisting of the product of a current into its conjugate force. On the left-hand side is the sum for the $\mathbf{J}_e, \mathbf{J}_s$ description, and on the right-hand side is the sum for the new $\mathbf{J}_e, \mathbf{J}_q$ description; the forces \mathbf{X}_e and \mathbf{X}_q , conjugate, respectively, to the new currents \mathbf{J}_e and \mathbf{J}_q , are yet to be found. The phenomenological equations for the new variables are

$$\mathbf{J}_e = M_{ee}\mathbf{X}_e + M_{eq}\mathbf{X}_q, \quad (10)$$

$$\mathbf{J}_q = M_{qe}\mathbf{X}_e + M_{qq}\mathbf{X}_q, \quad (11)$$

in which the identity of M_{eq} and M_{qe} is assured by virtue of (9). Substituting Eq. (8) for \mathbf{J}_q into (9) and collecting terms in \mathbf{J}_e and in \mathbf{J}_s we find

$$(\nabla\bar{\mu} + \mathbf{X}_e + \mu\mathbf{X}_q) \cdot \mathbf{J}_e + (\nabla T + T\mathbf{X}_q) \cdot \mathbf{J}_s = 0,$$

which is identically true for all \mathbf{J}_e and \mathbf{J}_s . Therefore, each quantity in parentheses vanishes and by solving the two resulting equations for the forces \mathbf{X}_e and \mathbf{X}_q we find

$$\mathbf{X}_e = -\nabla\bar{\mu} + (\mu/T)\nabla T, \quad (12)$$

$$\mathbf{X}_q = -(1/T)\nabla T. \quad (13)$$

The new phenomenological relations (10) and (11) become

$$\mathbf{J}_e = -M_{ee}\nabla\bar{\mu} - (1/T)(M_{eq} - \mu M_{ee})\nabla T, \quad (14)$$

$$\mathbf{J}_q = -M_{eq}\nabla\bar{\mu} - (1/T)(M_{qq} - \mu M_{eq})\nabla T, \quad (15)$$

where we have used the Onsager reciprocity relation $M_{eq} = M_{qe}$. These relations are completely equivalent to (3) and (4), and while they are no more nor less general than (3) and (4) they will be used later on to describe some of the thermoelectric effects from the viewpoint of an "energy of transport per particle" rather than from the viewpoint of an "entropy of transport per particle."

We wish next to relate the "M" coefficients with the "L" coefficients. Since the forces $-\nabla\bar{\mu}$ and $-\nabla T$ in the phenomenological relations are independently variable, the coefficients of each separate force in Eqs. (3) and (14) for \mathbf{J}_e must be identical; this leads to the following equations:

$$L_{ee} = M_{ee}, \quad (16)$$

$$TL_{es} = M_{eq} - \mu M_{ee}. \quad (17)$$

⁹ The concept of entropy transport is not a new one peculiar to the Onsager-Casimir theory. In fact, it was used in the older, so-called "pseudo-thermodynamic" theories, to which extensive references are given by de Groot in reference 2.