thermal electrical conductivity, a characteristic parameter of a given phase; Fourier's law, which says that the heat flow across a plane inside a phase without electrical current is proportional to the temperature gradient at the plane, the proportionality coefficient being the thermal conductivity for zero electrical current. Now when both an electrical current and a heat current flow simultaneously in a phase there is an interference or interaction between the two currents, and this interaction may be described by saying that each of the two flows can be caused in general by either or both of the two driving forces, i.e., temperature gradient and potential gradient. This interaction, and in fact this manner of expressing it, were known and introduced years before the Onsager theory was developed. But it was not until the development of this latter theory that it was found possible in a very general way to relate the proportionality or *interaction coefficients* with one another in such a fashion as to bring into the theory the several typical interference phenomena of thermoelectricity. The general way in which the interaction coefficients are related is based ultimately on statistical-mechanical considerations, and is finally expressed by a so-called reciprocity relation, or in our case by the simple equality of these two coefficients. In order for this equality relation to hold, however, it is necessary that the two linear relations[7] between the flows and the driving forces contain exactly the proper, conjugate flows and forces—any arbitrary, though physically reasonable choice of flow-force pairs will not necessarily form a proper, conjugate pair. It is probably this fact that prevented the earlier workers in irreversible thermodynamics from discovering the Onsager reciprocity relations empirically. The Onsager-Casimir theory furnishes general conditions to be met by the flow-force pairs in order that the reciprocity relations hold between coefficients, and subsequent developments have resulted in general formulas for conjugate forces and flows or currents applicable to a wide variety of problems. In any given problem involving interference between particle current and heat or energy current, for example, there are numerous choices of currents but once these are chosen there is no choice of conjugate forces. Similarly, it is often convenient to change over in a given problem to a new set of forces; this new choice of forces, however, dictates the choice of currents. Since the equations relating currents and forces are linear, it is always possible in a problem to transform from one set of currents to another set, if for example the use of a first set makes more physically understandable one aspect of the problem, while the use of a second set clarifies another aspect of the same problem. However, the transformation must satisfy a certain condition laid down by the theory. We shall see examples of this sort of thing in our discussion, but for a more satisfying treatment of the general theory the reader must consult either the original papers[8] or, say, de Groot's monograph[2] already mentioned. We want to emphasize the physical aspects of the theory as it applies to thermoelectricity, and shall therefore not give an extensive discussion of the general requirements which the force-current pairs must satisfy in order to be properly chosen. Instead, we simply select one particularly suitable set which is known to be conjugated, and proceed from this starting point. The general conditions on a force-current pair will then be stated and applied only briefly later on.

We have mentioned as one force and current pair the temperature gradient and heat flow current in Fourier's law, and as another pair the electrical potential gradient and the electrical current in Ohm's law. However, it is found that if one attempts to use both the temperature gradient ∇T and the electrical potential gradient $\nabla\phi$ as forces and both the electron (or particle) current $\mathbf{I}$ and heat current $\mathbf{J}_q$ as flows, the interaction coefficients are not identical; that is, in the two linear relations

$$\mathbf{I}=L_{11}\nabla\phi+L_{12}\nabla T,$$

$$\mathbf{J}_q=L_{21}\nabla\phi+L_{22}\nabla T,$$

the interaction coefficients L_{12} and L_{21} are not equal, and the equations are useless. But suppose that instead of writing Fourier's law in terms of a heat flow density and temperature gradient we write it in terms of an entropy flow density and a temperature gradient. The concept of an entropy flow vector may be described as follows. If we consider a plane inside a given phase with a temperature gradient, we can say that the entropy flow (density) across the plane at a particular point is equal to the absolute temperature at this point times the heat flow (density) across the plane at the same point. Or, from thermostatics we can write $\Delta Q=T\Delta S$, ΔQ representing heat added to a closed system across a unit area of its boundary and ΔS the corresponding "entropy added to the system at temperature T." If the heat and entropy "transfers" ΔQ and ΔS take place in a time Δt, then we can write $\Delta Q/\Delta t=T\Delta S/\Delta t$ or in the limit, $\mathbf{Q}=T\mathbf{S}$, the vectors now indicating flows of heat and entropy. Furthermore, suppose that in Ohm's law we use the gradient of the electrochemical potential instead of simply the electrical potential gradient. Finally, we may use either electrical current density $\mathbf{I}$ or *particle current density* $\mathbf{J}_e$, these being related in our case by $\mathbf{I}=-e\mathbf{J}_e$, where $-e$ is the electron charge. It turns out that for our problem involving the simultaneous flow of electrons and of entropy, the negative

[7] In a more complex problem involving ionic currents as well as electronic currents, there may be several particle currents in addition to an energy current, and a correspondingly larger number of driving forces. In such cases the Onsager reciprocity relations are most easily expressed by the symmetry $L_{ik}=L_{ki}$ of the matrix formed from all the proportionality coefficients. In our case we are considering electrons only so that we have two currents and two forces, and consequently two linear relations with $L_{12}=L_{21}$ when the flows and forces are properly chosen.

[8] L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931); Ann. N. Y. Acad. Sci. **46**, 241 (1945).