

The Application of Onsager's Reciprocal Relations to Thermoelectric, Thermomagnetic, and Galvanomagnetic Effects*

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Analysis of the thermoelectric, thermomagnetic, and galvanomagnetic effects by means of the reciprocal relations of Onsager leads to a simple and intuitive interpretation of the thermoelectric effects, provides a valid derivation of the Kelvin relations, and answers the long standing question as to the existence of relations among the effects in a magnetic field. It is shown that there exist two independent relations among the eight commonly defined coefficients in a magnetic field—one of these relations having been previously given by Bridgman. The nature of the second relation is discussed. Also, certain general observations on the applicability of the Onsager relations to steady-state processes are discussed.

INTRODUCTION

IN 1854 Lord Kelvin¹ proposed a "quasi-thermodynamic" method of analysis of the thermoelectric effects, leading to the well-known Kelvin relations. Although Kelvin himself carefully pointed out that his method was not completely justifiable, experiment confirmed the validity of the results obtained. The method was subsequently applied to the theory of electrolytic cells by Helmholtz² and to the Soret effect by Eastman,³ and was extended to the galvano- and thermomagnetic effects by Bridgman,⁴ in each case yielding important and correct relations. In 1931 Onsager⁵ revived the problem and proved a general and powerful set of reciprocal relations treating the symmetry in the mutual interference of two or more irreversible processes occurring simultaneously in a system. On the basis of these relations Onsager has specifically discussed diffusion processes⁶ and the flow of heat in anisotropic

crystals,⁵ and has pointed out that the whole class of results obtained by the quasi-thermodynamic method of Kelvin follows from the reciprocal relations. However, a treatment on this basis of the very important thermoelectric, thermomagnetic, and galvanomagnetic effects has not been given in the literature.**⁷⁻¹⁰ Such a treatment leads to a simple and intuitive interpretation of the thermoelectric effects in terms of an entropy flow per particle, provides a valid derivation of the Kelvin relations, and settles the long standing question as to the existence of relations among the effects in a magnetic field. It is shown that there are two independent relations among the eight commonly defined coefficients in a magnetic field—one of these relations having been previously given by Bridgman.

** However, Meixner (See reference 7.) has given both a detailed kinetic treatment of these effects, and some discussion of the results in the light of the Onsager relations. The effects have also been treated by the free-electron theory in a classic paper by Sommerfeld and Frank, (See reference 8.) and have recently been treated by Gurevich (See reference 9.) on the basis of an interaction between the electrons and phonons in the lattice. A thesis by DeGroot (See reference 10.) on the Soret effect, has very recently been brought to the author's attention. A part of the formalism of the present paper involving heat and entropy current densities appears also in DeGroot's work.

⁷ J. Meixner, *Ann. d. Physik* (5) **35**, 701 (1939); **36**, 105 (1939); **39**, 333 (1941); **40**, 165 (1941); **41**, 409 (1942); *Zeits. f. physik. Chemie* **B53**, 235 (1943).

⁸ A. Sommerfeld and N. H. Frank, *Rev. Mod. Phys.* **3**, 1 (1931).

⁹ L. Gurevich, *J. Phys. U.S.S.R.* **9**, 477 (1945); **10**, 67, 174 (1946).

¹⁰ S. R. DeGroot, Thesis, Eindhoven 1945; *L'Effet Soret* (N. V. Noord-Hollandsche Uitgevers Maatschappij, Amsterdam, 1945).

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I wish to take this opportunity to thank Professor L. Tisza, the director of the thesis, for extensive discussions and for many helpful suggestions.

¹ Lord Kelvin (Sir W. Thomson) *Collected Papers I* (University Press, Cambridge, 1882), pp. 232-291.

² H. v. Helmholtz, *Wiss. Abh.* **1**, 840 (1877).

³ E. D. Eastman, *J. Am. Chem. Soc.* **48**, 1482 (1926); **50**, 283 (1928); **50**, 292 (1928).

⁴ P. W. Bridgman, *Thermodynamics of Electrical Phenomena in Metals* (The Macmillan Company, New York, 1934).

⁵ L. Onsager, *Phys. Rev.* **37**, 405 (1931); **38**, 2265 (1931).

⁶ L. Onsager, *Ann. N. Y. Acad. Sci.* **XLVI**, 241 (1945).

I. ONSAGER'S RECIPROCAL RELATIONS

The reciprocal relations of Onsager express a certain symmetry in the mutual interference of two or more irreversible processes occurring simultaneously in a system. They follow from thermodynamic reasoning, plus the additional fact that, except in the presence of a magnetic or Coriolis force field, the laws of dynamics are symmetric with respect to future and past. The content of the relations may be briefly stated as follows:

Consider a set of irreversible processes, expressible as the rates of change of a set of measurable parameters, α_i , of the system. We shall assume these parameters to be even functions of the momenta of the particles composing the system.^{***,11} Assume also that the macroscopic laws which govern the processes (such as Ohm's law of electric conduction, Fick's law of diffusion, etc.) can be expressed in the linear forms

$$\delta\alpha_i/\delta t = \sum_j L_{ij}\gamma_j, \quad (1)$$

where

$$\gamma_j \equiv \delta S/\delta\alpha_j. \quad (2)$$

In equilibrium the entropy S is a maximum and the γ_j are therefore zero. Thus the γ_j are measures of the deviation from the equilibrium state. The L 's, or "kinetic coefficients," are functions of the state of the system, depending upon such variables as composition, temperature, and the values of applied magnetic or Coriolis force fields. If the L_{ij} were to be zero for all $i \neq j$, each "current" $\delta\alpha_j/\delta t$ would depend only on its own driving "force" γ_j , and the various processes could be considered as independent. Thus the quantity L_{ij} is a measure of the interference of the j th process on the course of the i th. Onsager's theorem now states that

$$L_{ij}(H) = L_{ji}(-H), \quad (3)$$

where H is the applied magnetic (or Coriolis) field. If no magnetic field is applied, Eq. (3) degenerates into the simple symmetry relation

$$L_{ij} = L_{ji}. \quad (4)$$

^{***} Casimir (See reference 11.) has shown that this is not a necessary restriction, and Onsager's theorem can be formulated in other cases. However, most common thermodynamic parameters (such as energy, volume, or number of particles) remain invariant if the directions of motion of all the particles are reversed, and for simplicity of statement we confine ourselves to this case.

¹¹ H. B. G. Casimir, *Rev. Mod. Phys.* **17**, 343 (1945).

The problem involved in the application of Onsager's relations to any particular set of processes is, of course, the identification of the proper "forces" γ_j . To do this directly from the defining equations (Eq. (2)) requires the knowledge of the caloric equation of state (i.e., of the entropy as a function of the variables α_j). It is, however, possible to avoid this by considering the rate of production of entropy rather than the entropy itself. We have, by a first-order Taylor expansion,

$$\delta S = \sum_j (\delta S/\delta\alpha_j)\delta\alpha_j = \sum_j \gamma_j \delta\alpha_j, \quad (5)$$

whence the rate of production of entropy associated with the irreversible process is

$$\delta S/\delta t = \sum_j \gamma_j (\delta\alpha_j/\delta t). \quad (6)$$

This equation provides a more convenient method for identifying the variables γ_j than does Eq. (2).

II. APPLICATION TO THERMOELECTRIC PROCESSES

By utilizing a procedure which might be called the "method of local equilibrium" we may apply the Onsager relations to steady-state processes, such as the thermoelectric processes.

The thermoelectric effects may be viewed as the result of the mutual interference of heat flow and electric current flow in a system, and we must now define appropriate current density vectors. The number of particles, the total internal energy, and the entropy of a system are definable thermodynamic variables. We define a particle current density \mathbf{J} , an energy current density \mathbf{W} , and an entropy current density \mathbf{S} , so that the divergence of each of these current densities is the rate of change per unit volume of the corresponding thermodynamic variable, and so that the current densities vanish in a vacuum.[†] In accordance with the familiar thermodynamic definition of heat, we are led to define a heat current density by

$$\mathbf{Q} \equiv T\mathbf{S}. \quad (7)$$

A steady-state process is characterized by the

[†] The condition that the currents vanish in a vacuum is necessary in order to remove the arbitrariness inherent in the definition in terms of a divergence. For a discussion of this matter see Casimir (reference 11).

conditions

$$\nabla \cdot \mathbf{W} = 0, \tag{8}$$

$$\nabla \cdot \mathbf{J} = 0, \tag{9}$$

and

$$\nabla \cdot \mathbf{S} = \dot{S}, \tag{10}$$

where \dot{S} is the rate of production of entropy per unit volume.

We may now employ the method of local equilibrium to evaluate $\nabla \cdot \mathbf{S}$. Let the actual system be approximated by a collection of small volume elements, each of which is in local equilibrium, and each of which has a distinct value of the temperature T and of the electrochemical potential μ . We shall discuss the validity of this approximation in Section III. Then, since each element is in equilibrium, we may apply to it the usual thermodynamic relations connecting the entropy, internal energy, and number of particles. Assuming no thermal expansion or other mechanical effects in the system (i.e., neglecting terms such as $P\delta V$), we may therefore write for the n th element

$$T_n \delta S_n = \delta U_n - \mu_n \delta N_n, \tag{11}$$

where S is the entropy, U is the total internal energy, and N is the number of particles. In accordance with our definitions of the current density vectors we thus obtain

$$T\mathbf{S} = \mathbf{W} - \mu\mathbf{J}, \tag{12}$$

or

$$\mathbf{Q} = \mathbf{W} - \mu\mathbf{J}. \tag{13}$$

Equation (13) identifies the heat current as the difference between the total energy current and the electrochemical potential energy current, and this agrees with our intuitive notion of heat as a kinetic energy current. Taking the divergence of Eq. (13) and recalling the conditions of a steady state (Eqs. (8) and (9)), we find

$$\nabla \cdot \mathbf{Q} = -\nabla \mu \cdot \mathbf{J}, \tag{14}$$

which states that the rate of increase in heat current is equal to the rate of decrease in the potential energy current.

The rate of production of entropy, \dot{S} , follows from Eq. (12) and the conditions for a steady state, Eqs. (8), (9), and (10):

$$\dot{S} = \nabla \cdot \mathbf{S} = \nabla \cdot \frac{1}{T} \cdot \mathbf{W} - \nabla \cdot \frac{\mu}{T} \cdot \mathbf{J} \tag{15}$$

or, using Eq. (13) to eliminate \mathbf{W} in favor of \mathbf{Q} ,

$$\dot{S} = \nabla \cdot \frac{1}{T} \cdot \mathbf{Q} - \frac{1}{T} \nabla \mu \cdot \mathbf{J}. \tag{16}$$

The interpretation of this equation is best brought out by using Eq. (14) to write

$$\dot{S} = \nabla \cdot \frac{1}{T} \cdot \mathbf{Q} + \frac{1}{T} \nabla \cdot \mathbf{Q}, \tag{17}$$

which states that the production of entropy is due to two causes: the first term is the production of entropy due to the flow of heat from high to low temperature, and the second term is the increase in entropy due to the degradation of electrochemical potential energy into heat.

We are now able to identify the proper "forces" for the application of Onsager's reciprocal relations. By comparing Eqs. (15) or (16) with Eq. (6), we find that if we take $-\mathbf{J}$ and \mathbf{W} as currents, the proper forces are $\nabla(\mu/T)$ and $\nabla(1/T)$, whereas if we take $-\mathbf{J}$ and \mathbf{Q} as currents, the proper forces are $(1/T)\nabla\mu$ and $\nabla(1/T)$. Accordingly, we may write the macroscopic laws governing the processes in the form

$$-\mathbf{J} = L_{11} \frac{1}{T} \nabla \mu + L_{12} \nabla \frac{1}{T}, \tag{18}$$

$$\mathbf{Q} = L_{21} \frac{1}{T} \nabla \mu + L_{22} \nabla \frac{1}{T},$$

and in the absence of an applied magnetic field, Onsager's theorem states that

$$L_{12} = L_{21}. \tag{19}$$

It is perhaps well to comment here on the nature of the electrochemical potential μ . We may consider μ to be composed of two parts, a chemical portion μ_c and an electrical portion μ_e .

$$\mu = \mu_c + \mu_e. \tag{20}$$

If the charge on a particle is e , then μ_e is simply $e\phi$, where ϕ is the ordinary electrostatic potential. The chemical potential μ_c is a function of the temperature and of the particle concentration. In an electrical conductor μ_e plays a minor role, and we fix our attention primarily on the e.m.f. $(1/e)\nabla\mu_e$. However, if we were to consider the diffusion of uncharged particles, $\nabla\mu_c$ would play the part of the driving force.

III. JUSTIFICATION OF THE APPLICATION TO STEADY-STATE PROCESSES

The derivation of the Onsager relations strictly refers only to a specific type of transient irreversible process, and the application of the relations to steady-state processes involves an approximation, the nature and validity of which we shall now examine.

The type of transient process to which the reciprocal relations primarily refer is that which occurs immediately following the lifting of a set of restraints, with respect to which the system is originally in equilibrium. The restriction to this type of process appears implicitly in the derivation given by Onsager in the nature of the averages taken over the statistical ensemble. However, many processes of interest are not of this transient nature, but occur in a steady state.

In Section II we have considered a method of application of the Onsager relations to steady-state processes, and we have seen that the approximation involved lies in the assumption that, for the purpose of calculating the entropy current, the system can be considered as the limiting case of many small sections, each in local equilibrium. In the language of statistical mechanics this is equivalent to the assumption that for the calculation of the entropy current the distribution function may be taken to be in the equilibrium form but with T and μ as functions of position. Actually, it is well known that the distribution function can be expressed as a function of this form plus a small deviation term.⁸ It is, of course, the smallness of this deviation term which is responsible for the excellence of the approximation made.

It will be recognized that the calculation of \mathbf{S} on the basis of the local-equilibrium distribution function is very similar to the procedure usually adopted in the application of Boltzmann's kinetic equation. This equation may be written as an equality between certain "flow terms" and certain "collision terms." In the calculation of the flow terms one may use the local-equilibrium value of the distribution function, but since the collision terms vanish in this approximation, it is necessary to include the deviation term in their calculation. Similarly, in our case, \mathbf{S} may be calculated on the basis of the local-equilibrium value of the distribution function, although a

direct statistical calculation of \dot{S} , which would vanish in this approximation, would require the inclusion of the deviation term.

Finally, we may mention that the kinetic laws governing the processes are themselves linear only in a similar approximation,¹² so that the reciprocal relations for steady-state processes are as valid as Ohm's law, Fick's law, etc.

IV. THERMOELECTRIC EFFECTS

We consider now a system in which a particle (or electric) current and a heat current flow parallel to the x axis, there being no applied magnetic field. Then, by Eqs. (18) and (19),

$$\begin{aligned} -\mathbf{J} &= L_{11} \frac{1}{T} \nabla \mu + L_{12} \nabla \frac{1}{T}, \\ \mathbf{Q} &= L_{12} \frac{1}{T} \nabla \mu + L_{22} \nabla \frac{1}{T}. \end{aligned} \quad (21)$$

The kinetic coefficients (the L 's) are properties of the medium considered, and are closely related to such familiar properties as the electric and heat conductivities. We shall see that the knowledge of the set of quantities L_{11} , L_{12} , and L_{22} is equivalent to the knowledge of the electric and heat conductivities and of the thermoelectric power of the medium.

The heat conductivity is defined as the heat current density per unit temperature gradient, for zero particle current.

$$\kappa \equiv -\mathbf{Q}/\nabla T \quad \text{for } \mathbf{J} = 0, \quad (22)$$

whence we find from the kinetic equations,

$$\kappa = \frac{1}{T^2 L_{11}} (L_{11} L_{22} - L_{12}^2) = \frac{D}{T^2 L_{11}}, \quad (23)$$

where we introduce the notation

$$D \equiv L_{11} L_{22} - L_{12}^2. \quad (24)$$

Similarly, the electric conductivity is defined as the electric current density ($e\mathbf{J}$) per unit potential gradient $[(1/e)\nabla\mu]$ in an isothermal system. It is easily seen that $(1/e)\nabla\mu$ is actually the e.m.f., for in a homogeneous isothermal system $\nabla\mu_e = 0$ and $\nabla\mu = \nabla\mu_e$. Thus

$$\sigma \equiv -e\mathbf{J} / \frac{1}{e} \nabla \mu \quad \text{for } \nabla T = 0, \quad (25)$$

¹² H. B. Callen, Thesis, M.I.T., 1947.

whence

$$\sigma = e^2 L_{11} / T. \tag{26}$$

In preparation for our application of the kinetic equations to practical experiments, we now note that the variables which can most easily be controlled independently by the experimenter are the particle (or electric) current density and the temperature gradient. We therefore find it convenient to express \mathbf{S} in terms of these variables. We thus obtain

$$\mathbf{S} = -\frac{L_{12}}{TL_{11}} \mathbf{J} + \frac{D}{TL_{11}} \nabla \frac{1}{T}. \tag{27}$$

According to this equation a current flowing in a conductor of a given temperature distribution carries with it an entropy per particle of $-L_{12}/TL_{11}$. This entropy flow is, of course, in addition to the entropy flow $(D/TL_{11})\nabla(1/T)$, which is independent of the particle current. The entropy flow per particle $-L_{12}/TL_{11}$ will prove to be such a useful quantity in the description of the thermoelectric effects that we introduce for it the special symbol S_J .

$$S_J \equiv -\frac{L_{12}}{TL_{11}}. \tag{28}$$

We shall see that $(1/e)S_J$ is equal to the thermoelectric power of the medium, so that, like κ and σ , it has direct physical significance as a property of the substance. The quantities κ , σ , and S_J have been expressed in terms of the kinetic coefficients, and conversely we have

$$\begin{aligned} L_{11} &= \frac{T}{e^2} \sigma, \\ L_{12} &= -\frac{T^2}{e^2} \sigma S_J, \\ L_{22} &= \frac{T^3}{e^2} \sigma S_J^2 + T^2 \kappa. \end{aligned} \tag{29}$$

We now consider the various thermoelectric effects in turn.

a—The Peltier Effect

The Peltier effect refers to the evolution of heat accompanying the flow of an electric current across an isothermal junction of two materials. Consider an isothermal junction of two con-

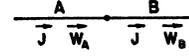


FIG. 1.

ductors A and B , and consider a current \mathbf{J} to be flowing. Then the total energy flow will be discontinuous across the junction, and the energy difference appears as “Peltier heat” at the junction. (See Fig. 1.) We have $\mathbf{W} = \mathbf{Q} + \mu \mathbf{J}$, and since both μ and \mathbf{J} are continuous across the junction it follows that the discontinuity in \mathbf{W} is equal to the discontinuity in \mathbf{Q} .

$$\mathbf{W}_A - \mathbf{W}_B = \mathbf{Q}_A - \mathbf{Q}_B.$$

Because of the isothermal condition the kinetic equations give, in either conductor,

$$\mathbf{Q} = TS_J \cdot \mathbf{J}, \tag{30}$$

whence

$$\mathbf{Q}_B - \mathbf{Q}_A = T \cdot (S_J^B - S_J^A) \cdot \mathbf{J}. \tag{31}$$

The Peltier coefficient Π_{AB} is defined as the heat which must be supplied to the junction when unit electric current passes from conductor A to conductor B . Thus,

$$\Pi_{AB} \equiv \frac{\mathbf{Q}_B - \mathbf{Q}_A}{e \mathbf{J}} = \frac{T}{e} (S_J^B - S_J^A). \tag{32}$$

The Peltier coefficient has the dimensions of an electromotive force, and is sometimes referred to as the Peltier e.m.f. This terminology must, however, be viewed as a mere figure of speech, for the potential μ is actually continuous at the junction.

We may regard the Peltier heat as supplying the discontinuity in the entropy flow per particle at the junction. For by Eq. (31)

$$\mathbf{S}_B - \mathbf{S}_A = (S_J^B - S_J^A) \cdot \mathbf{J} \tag{33}$$

so that a “Peltier entropy,” is equal to $(1/T)$. Peltier heat must be supplied at the junction.

b—The Thomson Effect

The Thomson effect refers to the evolution of heat as an electric current traverses a temperature gradient in a material. Because it is the only one of the three thermoelectric effects which deals with a single material, it is sometimes called the “homogeneous thermoelectric effect.”

Consider a conductor carrying a heat current, but no electric current. A temperature distribu-

tion governed by the temperature dependence of the kinetic coefficients (the L 's) will be set up. Let the conductor now be placed in contact at each point with a heat reservoir of the same temperature as that point, so that there is no heat interchange between conductor and reservoirs. Now, let an electric current pass through the conductor. Then a heat interchange will take place between conductor and reservoirs, this heat consisting of two parts—the Joule heat and the Thomson heat.

As the electric current passes along the conductor any change in total energy flow must be supplied by an energy interchange with the reservoirs. Thus, we must compute $\nabla \cdot \mathbf{W}$.

$$\nabla \cdot \mathbf{W} = \nabla \cdot (\mathbf{Q} + \mu \mathbf{J}) = \nabla \cdot \mathbf{Q} + \nabla \mu \cdot \mathbf{J}, \quad (34)$$

which may be expressed in terms of \mathbf{J} and $\nabla(1/T)$ by using Eqs. (7), (27), and (21):

$$\begin{aligned} \nabla \cdot \mathbf{W} = & -\nabla \left(\frac{L_{12}}{L_{11}} \right) \cdot \mathbf{J} - \nabla \cdot \left(\frac{D}{L_{11}} \frac{1}{T} \right) \\ & - \frac{T}{L_{11}} J^2 - \frac{TL_{12}}{L_{11}} \mathbf{J} \cdot \nabla \frac{1}{T}. \end{aligned} \quad (35)$$

However, the temperature distribution is that which is determined by the steady state with no electric current. Since $\nabla \cdot \mathbf{W} = 0$ in the steady state, Eq. (35) gives, with $\mathbf{J} = 0$,

$$\nabla \cdot \mathbf{W} = -\nabla \cdot \left(\frac{D}{L_{11}} \frac{1}{T} \right) = 0. \quad (36)$$

The term $\nabla \cdot [(D/L_{11})\nabla(1/T)]$ must therefore be zero even when $\mathbf{J} \neq 0$, for it depends on the temperature distribution only (it is apparent that the kinetic coefficients depend only on T and not on μ since the zero of μ is arbitrary, whereas the L 's are uniquely defined). We thus obtain

$$\nabla \cdot \mathbf{W} = -\nabla \left(\frac{L_{12}}{L_{11}} \right) \cdot \mathbf{J} - \frac{T}{L_{11}} J^2 - \frac{TL_{12}}{L_{11}} \mathbf{J} \cdot \nabla \frac{1}{T}, \quad (37)$$

and, writing

$$\nabla \left(\frac{L_{12}}{L_{11}} \right) = \frac{d}{dT} \left(\frac{L_{12}}{L_{11}} \right) \cdot \nabla T,$$

we have

$$\nabla \cdot \mathbf{W} = -\frac{T}{L_{11}} J^2 + T \frac{dS_J}{dT} \nabla T \cdot \mathbf{J}. \quad (38)$$

Since by Eq. (26) the electric conductivity is $\sigma = e^2(L_{11}/T)$ we recognize the first term above as the Joule heat. The second term therefore gives the Thomson heat. The Thomson coefficient τ is defined as the ratio of the Thomson heat absorbed to the product $\nabla T \cdot e\mathbf{J}$

$$\tau \equiv \frac{\text{Thomson heat}}{\nabla T \cdot e\mathbf{J}} = \frac{T dS_J}{e dT}. \quad (39)$$

It will be noted that the form of this equation suggests the analogy of τ to a specific heat [$= T(dS/dT)$], and, in fact, Thomson referred to τ as the "specific heat of electricity."

The details of the entropy transfer between conductor and reservoirs gives an interesting insight into the Thomson effect. We have

$$\mathbf{S} = S_J \cdot \mathbf{J} + \frac{D}{TL_{11}} \nabla \frac{1}{T}, \quad (27)$$

whence, by Eq. (36), we obtain

$$\nabla \cdot \mathbf{S} = \nabla S_J \cdot \mathbf{J} + \frac{D}{L_{11}} \left(\nabla \frac{1}{T} \right)^2. \quad (40)$$

However, the rate of production of entropy is

$$\dot{S} = -\frac{1}{T} \nabla \mu \cdot \mathbf{J} + \nabla \frac{1}{T} \cdot \mathbf{Q},$$

or, in terms of \mathbf{J} and $\nabla(1/T)$,

$$\dot{S} = \frac{1}{L_{11}} J^2 + \frac{D}{L_{11}} \left(\nabla \frac{1}{T} \right)^2. \quad (41)$$

Thus, the reservoirs at each point provide an input of entropy given by

$$\nabla \cdot \mathbf{S} - \dot{S} = -\frac{1}{L_{11}} J^2 + \nabla S_J \cdot \mathbf{J}, \quad (42)$$

which represents a Joule and a Thomson contribution. The Joule contribution extracts the entropy produced by the flow of current (Eq. (41)), and the Thomson contribution injects entropy to supply the flow of entropy per particle S_J (Eq. (40)).

c—The Seebeck Effect

The Seebeck effect refers to the production of an electromotive force in a thermocouple, under conditions of zero electric current.

Consider a thermocouple with junctions at temperatures T_1 and T_2 ($T_2 > T_1$). Let a voltmeter be inserted in the thermocouple at a point at which the temperature is T' . This voltmeter is to be such that it allows no passage of electricity, but offers no resistance to the flow of heat. We designate the two materials composing the thermocouple by A and B . (See Fig. 2.) With $\mathbf{J} = 0$ we obtain from the kinetic equations, for either conductor,

$$\nabla\mu = -S_J \nabla T. \tag{43}$$

Thus,

$$\mu_2 - \mu_1 = - \int_{T_1}^{T_2} S_J^A dT, \tag{44}$$

$$\mu_2 - \mu_{r'} = - \int_{T'}^{T_2} S_J^B dT, \tag{45}$$

$$\mu_{l'} - \mu_1 = - \int_{T_1}^{T'} S_J^B dT. \tag{46}$$

Eliminating μ_1 and μ_2 from these equations,

$$\mu_{r'} - \mu_{l'} = \int_{T_1}^{T_2} (S_J^B - S_J^A) dT. \tag{47}$$

But because there is no temperature difference across the voltmeter, the voltage is simply

$$V = \frac{1}{e} (\mu_{r'} - \mu_{l'}),$$

or

$$V = \frac{1}{e} \int_{T_1}^{T_2} (S_J^B - S_J^A) dT. \tag{48}$$

The thermoelectric power of the thermocouple, ϵ_{AB} , is defined as the change in voltage per unit change in temperature difference. The sign of ϵ_{AB} is chosen as positive if the voltage increment is such as to drive the current from A to B at the hot junction. Then

$$\epsilon_{AB} \equiv \frac{\partial V}{\partial T_2} = \frac{1}{e} [S_J^B(T_2) - S_J^A(T_2)]. \tag{49}$$

The quantities $(1/e)S_J^A$ and $(1/e)S_J^B$ are referred to as the thermoelectric powers of materials A and B , so that the entropy flow per

particle has a direct physical significance as a measurable property of the material.

d—The Kelvin Relations

The Kelvin relations connect the three thermoelectric coefficients. Recalling our values for these coefficients:

Peltier coefficient: $\Pi_{AB} = \frac{T}{e} (S_J^B - S_J^A), \tag{32}$

Thomson coefficient: $\tau = -\frac{T}{e} \frac{dS_J}{dT}, \tag{39}$

Thermoelectric power: $\epsilon_{AB} = \frac{1}{e} (S_J^B - S_J^A), \tag{49}$

we immediately obtain the Kelvin relations

$$\Pi_{AB} = T \epsilon_{AB}, \tag{50}$$

$$\tau_B - \tau_A = T \frac{d\epsilon_{AB}}{dT}. \tag{51}$$

V. THERMOMAGNETIC AND GALVANOMAGNETIC EFFECTS

If an external magnetic field is impressed upon a system in which a heat current and electric current simultaneously flow, several new effects appear. These effects have been discussed by Bridgman⁴ and by Sommerfeld and Frank,⁸ and there has been some speculation as to the existence of relations among the various effects. The application of Onsager's method results in the expression of all effects in terms of a number of independent kinetic coefficients, whence all relations among the effects may be obtained by algebraic elimination. We thus find that among the eight coefficients discussed by Sommerfeld and Frank there are two independent relations, one of which has been previously obtained by Bridgman.

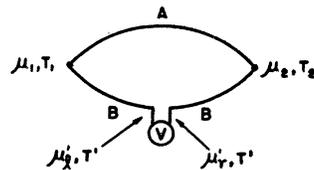


FIG. 2.

If we consider an isotropic system in which a magnetic field is applied parallel to the Z axis and in which the currents and gradients lie in the X - Y plane, we have again the equations

$$\mathbf{S} = \frac{1}{T} \mathbf{W} - \frac{\mu}{T} \mathbf{J}, \quad (52)$$

$$\mathbf{Q} \equiv T\mathbf{S} = \mathbf{W} - \mu\mathbf{J}, \quad (53)$$

$$\dot{S} = \nabla \cdot \frac{1}{T} \mathbf{Q} - \frac{1}{T} \nabla \mu \cdot \mathbf{J}, \quad (54)$$

and Eq. (54) may be written in component form:

$$\begin{aligned} \dot{S} = \nabla_x \frac{1}{T} \cdot Q_x + \nabla_y \frac{1}{T} \cdot Q_y \\ - \frac{1}{T} \nabla_x \mu \cdot J_x - \frac{1}{T} \nabla_y \mu \cdot J_y. \end{aligned} \quad (55)$$

This equation allows us to identify the four proper currents and the four proper forces for the application of Onsager's relations. In terms of these variables the kinetic equations become

$$\begin{aligned} -J_x &= L_{11} \frac{1}{T} \nabla_x \mu + L_{12} \nabla_x \frac{1}{T} + L_{13} \frac{1}{T} \nabla_y \mu + L_{14} \nabla_y \frac{1}{T}, \\ Q_x &= L_{21} \frac{1}{T} \nabla_x \mu + L_{22} \nabla_x \frac{1}{T} + L_{23} \frac{1}{T} \nabla_y \mu + L_{24} \nabla_y \frac{1}{T}, \\ -J_y &= L_{31} \frac{1}{T} \nabla_x \mu + L_{32} \nabla_x \frac{1}{T} + L_{33} \frac{1}{T} \nabla_y \mu + L_{34} \nabla_y \frac{1}{T}, \\ Q_y &= L_{41} \frac{1}{T} \nabla_x \mu + L_{42} \nabla_x \frac{1}{T} + L_{43} \frac{1}{T} \nabla_y \mu + L_{44} \nabla_y \frac{1}{T}. \end{aligned} \quad (56)$$

Because of the isotropy^{††} of the system, however, simple symmetry considerations require certain relations among the kinetic coefficients,

^{††} In order that our equations shall hold it is not necessary that the system be strictly isotropic, but only that there be isotropy in the X - Y plane and that the crystal symmetry be such that the currents and forces are coplanar (in the X - Y plane). It is of interest to note that physical isotropy in the X - Y plane is guaranteed by the Onsager relations if the crystallographic symmetry is such that the Z axis is a three-, four-, or six-fold rotation axis (cf. Onsager, reference 5).

and we clearly have

$$\begin{aligned} -J_x &= L_{11} \frac{1}{T} \nabla_x \mu + L_{12} \nabla_x \frac{1}{T} + L_{13} \frac{1}{T} \nabla_y \mu + L_{14} \nabla_y \frac{1}{T}, \\ Q_x &= L_{21} \frac{1}{T} \nabla_x \mu + L_{22} \nabla_x \frac{1}{T} + L_{23} \frac{1}{T} \nabla_y \mu + L_{24} \nabla_y \frac{1}{T}, \\ -J_y &= -L_{13} \frac{1}{T} \nabla_x \mu - L_{14} \nabla_x \frac{1}{T} + L_{11} \frac{1}{T} \nabla_y \mu + L_{12} \nabla_y \frac{1}{T}, \\ Q_y &= -L_{23} \frac{1}{T} \nabla_x \mu - L_{24} \nabla_x \frac{1}{T} + L_{21} \frac{1}{T} \nabla_y \mu + L_{22} \nabla_y \frac{1}{T}, \end{aligned} \quad (57)$$

where, furthermore, L_{11} , L_{12} , L_{21} , and L_{22} are even functions of the magnetic field and where L_{13} , L_{14} , L_{23} , and L_{24} are odd functions of the magnetic field.

We may now impose the Onsager relation

$$L_{ij}(H) = L_{ji}(-H), \quad (58)$$

and thus obtain

$$\begin{aligned} -J_x &= L_{11} \frac{1}{T} \nabla_x \mu + L_{12} \nabla_x \frac{1}{T} + L_{13} \frac{1}{T} \nabla_y \mu + L_{14} \nabla_y \frac{1}{T}, \\ Q_x &= L_{12} \frac{1}{T} \nabla_x \mu + L_{22} \nabla_x \frac{1}{T} + L_{14} \frac{1}{T} \nabla_y \mu + L_{24} \nabla_y \frac{1}{T}, \\ -J_y &= -L_{13} \frac{1}{T} \nabla_x \mu - L_{14} \nabla_x \frac{1}{T} + L_{11} \frac{1}{T} \nabla_y \mu + L_{12} \nabla_y \frac{1}{T}, \\ Q_y &= -L_{14} \frac{1}{T} \nabla_x \mu - L_{24} \nabla_x \frac{1}{T} + L_{12} \frac{1}{T} \nabla_y \mu + L_{22} \nabla_y \frac{1}{T}. \end{aligned} \quad (59)$$

Thus there are just six independent kinetic coefficients. The coefficients L_{11} , L_{12} , and L_{22} are even functions of the magnetic field, while the coefficients L_{13} , L_{14} , and L_{24} are odd functions of the magnetic field.

We may now consider in turn the various coefficients defined by Sommerfeld and Frank. The definitions of the various effects are self-explanatory, and we give the appropriate coefficients in terms of the kinetic coefficients, as obtained by application of the kinetic Eqs. (59).

a—The Isothermal Electric Conductivity

The isothermal value of the electric conductivity is obtained if the system is constrained to maintain a uniform temperature. Thus

$$\sigma_i \equiv -eJ_x / \frac{1}{e} \nabla_x \mu \quad (60)$$

under the conditions

$$\nabla_x T = \nabla_y T = J_y = 0, \quad (61)$$

whence

$$\sigma_i = \frac{e^2}{TL_{11}} (L_{11}^2 + L_{13}^2). \quad (62)$$

b—The Adiabatic Electric Conductivity

The adiabatic value of the electric conductivity is obtained if the system is so arranged that no transverse currents can flow, although transverse gradients are allowed to develop. Thus

$$\sigma_a \equiv -eJ_x / \frac{1}{e} \nabla_x \mu, \quad (63)$$

under the conditions

$$\nabla_x T = Q_y = J_y = 0, \quad (64)$$

whence

$$\sigma_a = \frac{e^2}{TD} \begin{vmatrix} L_{11} & L_{13} & L_{14} \\ -L_{13} & L_{11} & L_{12} \\ -L_{14} & L_{12} & L_{22} \end{vmatrix}, \quad (65)$$

where

$$D = L_{11}L_{22} - L_{12}^2.$$

c—The Isothermal Heat Conductivity

$$\kappa_i \equiv -Q_x / \nabla_x T, \quad (66)$$

under the conditions

$$J_x = J_y = \nabla_y T = 0, \quad (67)$$

whence

$$\kappa_i = \frac{1}{T^2} \frac{1}{L_{11}^2 + L_{13}^2} \begin{vmatrix} L_{11} & L_{13} & L_{14} \\ -L_{13} & L_{11} & L_{12} \\ -L_{14} & L_{12} & L_{22} \end{vmatrix}. \quad (68)$$

d—The Adiabatic Heat Conductivity

$$\kappa_a \equiv -Q_x / \nabla_x T, \quad (69)$$

under the conditions

$$J_x = J_y = Q_y = 0, \quad (70)$$

whence

$$\kappa_a = \frac{1}{T^2} \begin{vmatrix} L_{11} & L_{12} & L_{13} & L_{14} \\ L_{12} & L_{22} & L_{14} & L_{24} \\ -L_{13} & -L_{14} & L_{11} & L_{12} \\ -L_{14} & -L_{24} & L_{12} & L_{22} \end{vmatrix} \begin{vmatrix} L_{11} & L_{13} & L_{14} \\ -L_{13} & L_{11} & L_{12} \\ -L_{14} & L_{12} & L_{22} \end{vmatrix}^{-1} \quad (71)$$

e—The Isothermal Hall Effect

$$(\text{Hall})_i \equiv \frac{1}{e} \nabla_y \mu / HeJ_x, \quad (72)$$

under the conditions

$$J_y = \nabla_y T = \nabla_x T = 0, \quad (73)$$

whence

$$(\text{Hall})_i = -\frac{T}{e^2 H} \frac{L_{13}}{L_{11}^2 + L_{13}^2} \quad (74)$$

It should be noted that the adiabatic Hall coefficient, defined as the transverse e.m.f. per unit electric current and per unit magnetic field, cannot be obtained from our equations. For in the adiabatic effect we do not have $\nabla_y T = 0$ and therefore $(1/e)\nabla_y \mu \neq$ e.m.f. The adiabatic Hall coefficient is, however, the more commonly measured of the two Hall coefficients.

f—The Isothermal Nernst Effect

$$(\text{Nernst})_i = -\frac{1}{e} \nabla_y \mu / H \nabla_x T, \quad (75)$$

under the conditions

$$J_x = J_y = \nabla_y T = 0, \quad (76)$$

whence

$$(\text{Nernst})_i = \frac{1}{eHT} \frac{L_{11}L_{14} - L_{12}L_{13}}{L_{11}^2 + L_{13}^2}. \quad (77)$$

g—The Ettingshausen Effect

$$(\text{Ettingshausen}) \equiv \nabla_y T / H e J_x \quad (78)$$

under the conditions

$$J_y = Q_y = \nabla_x T = 0, \quad (79)$$

whence

$$(\text{Ettingshausen}) = \frac{T^2}{eH} (L_{11}L_{14} - L_{12}L_{13}) \cdot \begin{vmatrix} L_{11} & L_{13} & L_{14} \\ -L_{13} & L_{11} & L_{12} \\ -L_{14} & L_{12} & L_{22} \end{vmatrix}^{-1} \quad (80)$$

h—The Leduc-Righi Effect

$$(\text{Leduc-Righi}) \equiv \nabla_y T / H \nabla_x T \quad (81)$$

under the conditions

$$J_x = J_y = Q_y = 0, \quad (82)$$

whence

$$(\text{Leduc-Righi}) = \frac{1}{H} \cdot \begin{vmatrix} L_{11} & L_{13} & -L_{12} \\ -L_{13} & L_{11} & L_{14} \\ -L_{14} & L_{12} & L_{24} \end{vmatrix} \cdot \begin{vmatrix} L_{11} & L_{13} & L_{14} \\ -L_{13} & L_{11} & L_{12} \\ -L_{14} & L_{12} & L_{22} \end{vmatrix}^{-1} \quad (83)$$

i—Relations Among the Coefficients

We have eight coefficients expressed in terms of six independent kinetic coefficients, and it is apparent, therefore, that there exist two independent relations among these coefficients. One

relation, attributable to Bridgman, may be easily verified to be

$$T \cdot (\text{Nernst})_i = \kappa_i \cdot (\text{Ettingshausen}). \quad (84)$$

Because the coefficients of the various effects involve third or fourth powers of the kinetic coefficients, it proves impractical to obtain the second relation in an explicit algebraic form, but the expressions for the coefficients of the effects may be considered to be a parametric statement of this relation. We may see also, by considering the field dependence of the coefficients, that this second relation, unfortunately, is of less practical significance than is Bridgman's relation (84). We have seen that L_{13} , L_{14} , and L_{24} are odd functions of the field, and L_{11} , L_{12} , and L_{22} are even functions. It follows that all the coefficients of the various effects are even functions of the magnetic field, which is also evident physically. If, now, we consider only the field-independent term in the coefficients of the effects, we find the relations

$$\kappa_i^0 = \kappa_a^0, \quad (85)$$

$$\sigma_i^0 = \sigma_a^0, \quad (86)$$

$$T \cdot (\text{Nernst})_i^0 = \kappa_i^0 \cdot (\text{Ettingshausen})^0 \quad (87)$$

and no others. Thus, even for small fields, the Bridgman relation has an independent significance, whereas the second relation degenerates into the comparatively trivial Eqs. (85) and (86). Since measurements are ordinarily made in the range in which no distinction is made between κ_i and κ_a or σ_i and σ_a , we thus see that the second relation introduces no practically significant results for this small-field type of measurement.