A NEW KIND OF e.m.f. AND OTHER EFFECTS THERMODYNAMICALLY CONNECTED WITH THE FOUR TRANSVERSE EFFECTS

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Abstract

The Hall e.m.f. attending a current in a magnetic field is subjected to a thermodynamic analysis like that for an ordinary battery, from which it appears that if the Hall e.m.f. has a temperature coefficient, there must be a reversible heating effect when a transverse current flows across a conductor carrying a longitudinal current in a magnetic field. But other arguments show that this heating effect vanishes, and furthermore, it could not be found experimentally. The consequent vanishing of the temperature coefficient of the Hall e.m.f. involves the existence of a new sort of e.m.f., that is, an e.m.f. in a conductor carrying a current in which the temperature is uniformly changing. Corresponding analysis may be made for the other transverse effects. A thermo-motive force connected with the Righi-Leduc coefficient exists in a conductor carrying a thermal conduction current when its temperature changes uniformly. Other relations are deduced connecting the Nernst coefficient and the Ettingshausen coefficient with the new e.m.f. and thermo-motive force. It appears that the temperature dependence of all these quantities is simply connected, and in particular, that the temperature coefficient of the Hall coefficient vanishes at 0°K. The new relations show that certain relations suggested in a previous paper from general considerations of a non-thermo-dynamic character cannot be rigorously exact. A new account is given of the origin of the major part of the Ettingshausen temperature gradient, which is approximately checked by experiment. Finally, the order of magnitude of various small effects is discussed. It is a thermodynamic consequence of the existence of a temperature e.m.f. that there is a temperature change when the current in a conductor changes in magnitude, but it is far below experimental reach. It must be recognized that the specific heat of a conductor is altered by the presence of an electric current. The specific heat is also altered by the presence of an ordinary thermal conduction current. Numerical considerations suggest that the proper velocity to be associated with the thermal current, whether ordinary conduction current, or thermal current convected by an electrical current, is the velocity of sound.

THERE has been so much speculation about the detailed functioning of the mechanisms which may be responsible for the four transverse effects, namely the Hall, Ettingshausen, Nernst, and Righi-Leduc effects, and the whole subject is still in such an unsettled state, that it is well to obtain by arguments of a thermodynamic or other general character all the information which we can which must be independent of any special mechanism. It is not inconceivable that a better understanding of the thermodynamic connections between these effects may lead to a better understanding of the effects themselves. It is surprising how little this method of attack has been used in the past and there are still simple relations of a thermodynamic character which apparently have not been noticed. Practically the only previous applications of thermodynamics to this subject have been made by Lorentz and myself,[1] but there are still other relations not hitherto touched.

Relations of a purely thermodynamic character may be obtained by constructing electromagnetic or thermodynamic engines utilizing the various effects to furnish energy. Consider first the Hall effect. An electric current flows in a toroid of mean radius a, breadth b, and depth d, breadth and depth being small compared with a. There is a uniform magnetic field of strength H prependicular to the plane of the toroid. The magnetic field may be supposed produced by a permanent magnet with zero temperature coefficient. The circuit is supposed resistanceless, and in the following, irreversible effects arising from the Joulean heating are neglected. This is allowable, because by increasing the linear dimensions of the circuit indefinitely, keeping the total current I constant, the electromagnetic energy of the circuit, $\frac{1}{2}LI^2$, may be made indefinitely large compared with the Joulean dissipation of energy in unit time, RI^2, since L increases in direct proportion to the linear dimensions, and R decreases in the same ratio.

The inner and outer circumferences of the toroid are at a difference of potential in virtue of the Hall effect. If we short circuit across from the inner to the outer circumference, a uniform radial current will flow; this current may be used to drive an external electromagnetic engine, and so energy may be taken out of the system. The external electromagnetic engine may be assumed perfectly efficient, so that the energy output is the product of the Hall potential difference and the amount of electricity flowing transversely. The source of the energy output is primarily the energy of self induction, $\frac{1}{2}LI^2$, associated with the primary current, and the mechanism by which this energy is tapped is the Hall e.m.f. associated with the transverse flow acting circumferentially in the toroid and opposing the primary current. This arrangement is for thermodynamic purposes indistinguishable from a battery, and the ordinary analysis for a battery applies. In particular, if the Hall e.m.f. depends on temperature, then, in analogy with the known behavior of ordinary cells, we may expect reversible heating effects when the transverse current flows. The analysis is so simple that it will pay to reproduce it from the beginning.

Call I the total current, and i the current density, where $I = bdi$. Then the definition of the Hall coefficient at once gives:

$$\text{Transverse e.m.f.} = bHiR,$$

where R is the Hall coefficient, using the conventional notation. If a transverse quantity of electricity dq_e flows, the work done is the product of quantity and e.m.f., or

$$dW = bHiRdq_e.$$

The only variables in this system capable of external manipulation are temperature and transverse flow, which are therefore to be taken as the independent variables. The conservation of energy now gives at once:

[1] H. A. Lorentz, Report of the Fourth Solvay Congress, Conductibilité Électrique des Metaux, 1924, pp. 354–360; P. W. Bridgman, Phys. Rev. **24**, 644–651 (1924).

$$dQ = \left(\frac{\partial E}{\partial \tau}\right)_{q_e} d\tau + \left(\frac{\partial E}{\partial q_e}\right)_\tau dq_e + bHiRdq_e,$$

where E is internal energy and Q heat absorbed. Now form $dS = dQ/\tau$, and write down the condition that dS be a perfect differential, by equating the cross derivatives of the coefficients of $d\tau$ and dq_e. This gives at once, neglecting the thermal expansion of the material of the toroid,

$$\left(\frac{\partial Q}{\partial q_e}\right)_\tau = \tau bH \frac{\partial}{\partial T}(iR). \tag{1}$$

This indicates that when a transverse current flows in a conductor arranged to show the Hall effect there is a reversible generation of heat required to maintain the system isothermal.

In Eq. (1), Q and q_e are the total amounts of heat and flow of electricity respectively. If Q' is the development of heat per unit volume, we have approximately $Q = 2\pi abdQ'$, and if dq_e' is the density of transverse flow, we have $dq_e = 2\pi dadq_e'$. This gives:

$$\left(\frac{\partial Q'}{\partial q_e'}\right)_\tau = \tau H \frac{\partial}{\partial \tau}(iR)_{q_e}, \tag{2}$$

an equation exhibiting the thermal effect in terms of intrinsic properties of the materials, independent of the dimensions of the circuit.

We now have to consider the term $\partial/\partial\tau(iR)_{q_e}$ on the right hand side of the equations. Expanded, this is $i(\partial R/\partial\tau)q_e + R(\partial i/\partial\tau)_{q_e}$. Numerically the proportional change of R for one degree for bismuth, for example, is 0.004. The term $(\partial i/\partial\tau)_{q_e}$ one would probably say on first impulse to be zero, since this denotes the change of current produced by a change of temperature acting so quickly that the Joulean effects may be neglected, and with no transverse flow, that is, with no extraction of work from the system. If the term were not zero, this would demand that there be an e.m.f. in a circuit in which the temperature is changing, and this is an effect not usually considered. I believe, however, that this e.m.f. must exist. My reason is that there are at least two arguments which demand that the absorption of heat accompanying transverse flow be zero, and the only way in which this is reconcilable with the thermodynamic expressions above is that

$$\frac{\partial}{\partial\tau}(iR) \equiv 0, \text{ or } \frac{1}{i}\frac{\partial i}{\partial\tau} = -\frac{1}{R}\frac{\partial R}{\partial\tau} \neq 0.$$

The first argument is derived from the vector character of the current. The transverse and longitudinal currents combine according to the ordinary rules for vectors into a single current, and such a current flowing in a magnetic field is without heating effect, according to original assumption, as far as known experimentally, and also in accordance with the demands of symmetry. The relations here are somewhat simplified by imagining the conductor in the form of a cross, the longitudinal and transverse currents combining at the center of the cross as indicated to a sufficient degree of approximation in Fig. 1. The only way of saving the situation seems to be to assume that the heating effect is localized in the periphery of the central square, where the direction of current flow changes, as indicated by the dotted lines. But this is inconsistent with the dimensions of the effect as shown by Eq. (2) which exhibits the effect as a heating per unit volume, whereas if the effect were concerned with the change of direction, it would be an effect per unit area.

The second argument is derived from the symmetry of the longitudinal and transverse currents. It is evident in the first place that the heating effect

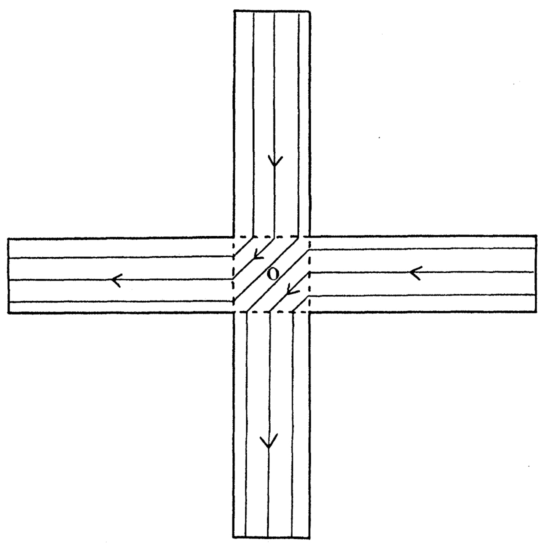

Fig. 1.

of Eq. (2) can be exhibited as a heating effect per unit time per unit transverse current. But if the arrangement is geometrically symmetrical in longitudinal and transverse current, as may be accomplished by making the conductor in the form of a cross as in Fig. 1, then the same result should be obtained independently of which current is called transverse and which longitudinal. An inspection of the figure shows that the symmetry relations make this impossible, for calling the transverse current longitudinal and conversely demands that the effect reverses sign. The only quantity equal to its own negative is zero, showing again that the heating effect must vanish.

There is apparently, therefore, an e.m.f. in a conductor in which the temperature is changing such that

$$\frac{1}{i}\frac{\partial i}{\partial \tau} = -\frac{1}{R}\frac{\partial R}{\partial \tau}.$$

The partial derivative in i may be taken to have the general significance that no work is to be extracted from the system during the change of temperature;

the partial derivative in R may for practical purposes be taken to be the ordinarily determined temperature derivative.

The experimentally determined values of $(1/R)(\partial R/\partial\tau)$ are so large, 0.004 for bismuth, that the related e.m.f. cannot be treated as a negligibly small quantity. An approximate expression for this e.m.f. may be readily found. To get it, we neglect any interaction between the thermal and the electrodynamic energy of the system, setting the total internal energy equal to the sum of the ordinary internal thermal energy in the absence of the current plus the electrodynamic energy, $\frac{1}{2}LI^2$. This amounts to assuming that the specific heat of a conductor carrying a current is the same as that of the same conductor without the current. Later in this paper an estimate will be made of the order of magnitude of this small effect. Utilizing this approximation, the e.m.f. arising from a change of temperature changes only the electrodynamic energy of the system, and we have:

$$\frac{d}{dt}[\tfrac{1}{2}LI^2] = I \times \text{e.m.f.},$$

whence at once:

$$\text{e.m.f.} = L\frac{dI}{dt} = L\frac{\partial I}{\partial\tau}\frac{d\tau}{dt}\cdot$$

But $(1/I)(\partial I/\partial\tau) = (1/i)(\partial i/\partial\tau)$, so that $\partial I/\partial\tau = -I(1/R)(\partial R/\partial\tau)$, and

$$\text{e.m.f.} = -\left(LI\frac{1}{R}\frac{\partial R}{\partial\tau}\right)\frac{\partial\tau}{dt}\cdot \qquad (3)$$

That is, the temperature e.m.f. in a circuit in which the temperature is changing at unit rate is $-LI(1/R)(\partial R/\partial\tau)$.

One can see in a general way why there should be an effect of this kind. In the first place, it arises from the magnetic field of the current on itself, the external magnetic field having dropped out of the picture. That the external field ought to have no net effect is suggested by the theorem of elementary electrodynamic theory that there is no mutual energy between an electrical current and a system of permanent magnets. Some of the electrons which constitute the current will move perpendicular to the magnetic field of the current itself, and will thus experience an action in virtue of the Hall effect which will have a component along the original current. The intensity of this action involves the self magnetic field, which explains how L gets into the picture. Furthermore, the number and distribution of the transversely moving electrons is a function of the temperature, so that there will be an interaction, manifesting itself as an e.m.f., when temperature changes. To give a detailed account of this effect from the statistical point of view would probably be prohibitively complicated, and would involve integration over the entire conductor of many terms, a number of which would drop out from the final result.

An experimental attempt was made to detect the existence of the transserve heating effect, when I first noticed the analogy with an ordinary battery, and had not yet realized that the relations between other quantities were such as to make this zero. Two crosses of bismuth like Fig. 1 were cast, the arms being about 1.2 by 0.6 cm in section. In casting, they were chilled rapidly from the molten condition so as to make the crystal structure as fine grained as possible. These crosses were mounted face to face, separated by a layer of cellophane for insulation, and the two junctions of a copper-constantan thermocouple were attached to the two centers of the crosses, indicated by 0 in the figure. The couple indicated, therefore, the differential effect at the centers of the two crosses. The electrical connections were such that the currents in the various branches could be varied independently, both as to magnitude and direction. The magnetic field was about 5000 gauss, and the maximum current density about 10 amperes per square cm. The difficulty with the experiment is in eliminating the effect of the finite size of the crystal grains. Because of the unequal resistance of the grains in different directions, the current experiences many internal changes of direction. Each of these is accompanied by a local heating effect, in virtue of the internal Peltier heat. This is changed by the application of a magnetic field, because of the effect of the field on the resistance. Effects of this kind exist with only a longitudinal current. However, by using all possible combinations of currents, and noting that some of the effects change sign when current direction changes and some do not, it was possible to show that if any heating effect of the kind corresponding to Eq. (2) exists it must be less than 10 percent of that part of the non-isotropic effects which is due to the action of the magnetic field. Numerically, this meant that any final shift of equilibrium of temperature due to the effect sought was less than 0.006°. This was much less than a preliminary calculation had indicated was to be expected on the assumption that $\partial i/\partial\tau = 0$. This is probably as good a proof of the non-existence of the effect as can be given without very much more elaborate precautions. It was a great surprise to find that the magnetic influence on the internal non-isotropic effects was so large. It raises the question whether such effects have been sufficiently considered in previous measurements; measurements of the Ettingshausen temperature difference would be particularly susceptible to error from this source.

Returning now to the relation $(\partial/\partial\tau)(iR) = 0$, we can derive a suggestion as to the behavior of R at 0° K. It seems highly probable that the e.m.f. arising from change of temperature vanishes at 0°K. We would expect this from general considerations suggested by experience with the third law, and the mechanistic explanation of this e.m.f. just given would suggest the same thing. For the transverse components of motion of the electrons which constitute the current would be expected to lose all their haphazard quality at low temperatures, and therefore their capacity for taking part in thermal effects. If $\partial i/\partial\tau$ vanishes at 0°K, this demands:

$$\lim_{\tau=0} \frac{1}{R}\frac{\partial R}{\partial \tau} = 0.$$

This relation appears to be consistent with the experimental results found at Leiden,[2] although the experimental accuracy is not always great enough to give perfectly definite indications.

The other transverse effects may now be subjected to an analysis similar to that above for the Hall effect. In doing this it will be convenient to introduce new coefficients in place of the conventional Nernst and Righi-Leduc coefficients, since the conventional definitions of these involve a lack of symmetry as compared with the Hall and Ettingshausen coefficients. The conventional Nernst coefficient, Q_N is to be replaced by Q_N' where $Q_N' = Q_N/k$, k being the thermal conductivity, and the conventional Righi-Leduc coefficient S_R is to be replaced by S_R', where $S_R' = S_R/k$. These coefficients are written with subscripts N and R to avoid confusion with the thermodynamic symbols Q for quantity of heat and S for entropy. These altered definitions now give the following consistent scheme for the four transverse effects:

(1) Hall transverse potential gradient with longitudinal electric current, $i, = RHi$.

(2) Ettingshausen transverse temperature gradient with longitudinal electric current, $i, = PHi$.

(3) Nernst transverse potential gradient with longitudinal heat current, $w, = Q_N'Hw$.

(4) Righi-Leduc transverse temperature gradient with longitudinal heat current, $w, = S_R'Hw$.

i and w are here density of electrical and thermal current.

Imagine now the toroid of the preceding analysis with a circumferential heat current replacing the electrical current. The ring will have to be split along some radius and the two sides of the slit maintained at a difference of temperature. This temperature difference is to be maintained irrespective of how the mean temperature of the whole system may change. The irreversible effects connected with thermal conduction in such a system may be neglected by making all changes in the system rapidly, so that the dissipation due to the thermal conduction is vanishingly small compared with other effects.

The exact parallel of the preceeding analysis for the Hall effect may now be made. Allow a quantity of heat dq_w to flow transversely, and utilize this to drive a thermodynamic engine working between the temperature limits of the Righi-Leduc temperature difference. This difference is $S_R'bHw$, and the work received from the engine is:

$$dW = \frac{1}{\tau} S_R'bHwdq_w.$$

The source of this work is the work done by the longitudinal heat current in flowing through the longitudinal Righi-Leduc temperature difference accompanying the flow of the transverse heat current. A result exactly similar to that before follows at once on writing down the condition that the entropy change be a perfect differential, namely:

[2] Bengt Beckman, Leiden Communications, Supplement, No. 40, 1915.

$$\left(\frac{\partial Q}{\partial q_w}\right)_\tau = \tau b H \frac{\partial}{\partial \tau}\left(\frac{w S_R'}{\tau}\right),$$

or this may be written as heat per unit volume in terms of densities:

$$\left(\frac{\partial Q'}{\partial q_w'}\right)_\tau = \tau H \frac{\partial}{\partial \tau}\left(\frac{w S_R'}{\tau}\right). \tag{4}$$

Exactly the same arguments as applied before, namely one from combining longitudinal and transverse heat currents vectorially, and one from the effect of interchanging longitudinal and transverse currents, may be applied to this case, showing that this heating effect must vanish, giving the relation $\partial/\partial\tau(wS_R'/\tau)=0$, or:

$$\frac{1}{\frac{S_R'}{\tau}} \frac{\partial}{\partial \tau}\left(\frac{S_R'}{\tau}\right) = -\frac{1}{w}\frac{\partial w}{\partial \tau}. \tag{5}$$

It is to be presumed that S_R'/τ varies with temperature, and that therefore the term $(1/w)(\partial w/\partial\tau)$ exists. This is the formal analogue of the expression $(1/i)(\partial i/\partial\tau)$, and denotes a change in a thermal current when the mean temperature is changed, no external work being taken from the heat current and the change being made so rapidly that the dissipation of the thermal stream against thermal resistance is negligible. Such phenomena connected with thermal currents certainly have not been detected, and the mechanism must be quite different from that in the electrical case. An electrical current is capable of coasting for a certain time after the e.m.f. has ceased, driven by the stored energy of self induction. The strict analogue of self induction does not exist for a thermal current. If, however, the thermal current is at all like ordinary currents in having a property analogous to velocity, it must also have a space density, so that the energy content and therefore the specific heat of a body carrying a thermal current is different from that of an equivalent assembly of infinitesimal elements with no thermal current. This space density of energy may perform the same function as the energy of self induction of an electrical current, and give meaning to the derivative $\partial w/\partial\tau$. An estimate will be made later of the order of magnitude of such effects. They are too small to be detected by direct experiment, but we may nevertheless recognize their existence and use them in theoretical discussion.

The other two effects, the Ettingshausen and Nernst effects may be similarly analyzed. By allowing a transverse heat current to flow in the presence of a longitudinal electrical current, energy may be taken out of the system in virtue of the Ettingshausen transverse temperature difference, and by allowing electricity to flow transversely in the presence of a longitudinal heat current energy may be taken out in virtue of the Nernst transverse potential difference. The same analysis as before demands accompanying heat effects, which, written for unit volume, are respectively:

$$\left(\frac{\partial Q'}{\partial q_w'}\right)_\tau = \tau H \frac{\partial}{\partial \tau}\left(\frac{iP}{\tau}\right) \tag{6}$$

$$\left(\frac{\partial Q'}{\partial q_e'}\right)_\tau = \tau H \frac{\partial}{\partial \tau}(wQ_N'). \tag{7}$$

We expect as before that these two effects are zero in virtue of other relations. The argument has to be somewhat modified, however. The first argument disappears entirely, because a heat current and an electric current do not combine vectorially. The second argument may, however, be appropriately modified. It is to be noticed in the first place that there is a reciprocal relation between the sources of the energy of the phenomena involved in Eqs. (6) and (7). The energy extracted by the transverse thermal flow of Eq. (6) is provided by the longitudinal electric current flowing against the Nernst e.m.f. acting longitudinally associated with the transverse heat current. Similarly, the energy extracted by the transverse electric flow of Eq. (7) has its source in the longitudinal heat current flowing against the Ettingshausen temperature difference acting longitudinally associated with the transverse electric flow. Eq. (6) now demands that dQ' be positive when the transverse heat current extracts energy from the longitudinal electric current, and (7) demands a positive dQ' when the transverse electric current extracts energy from the longitudinal heat current. But the situation of Eq. (6) may also be described as a longitudinal heat current in the presence of a transverse electric current, and the energy relations demand that the transverse electric current give energy to the longitudinal heat current. We thus again have the dilemma of a quantity equal to its own negative, and the only way out is the quantity itself to vanish. Hence

$$\frac{\partial}{\partial \tau}\left(\frac{iP}{\tau}\right) = 0 \tag{8}$$

and

$$\frac{\partial}{\partial \tau}(wQ_N') = 0. \tag{9}$$

The $\partial i/\partial \tau$ which occurs in (8) is the same as that which occurred in connection with the Hall coefficient, and the $\partial w/\partial \tau$ of (9) is the same as in the expression for the Righi-Leduc coefficient. Eliminating these derivatives gives:

$$\frac{1}{\frac{P}{\tau}} \frac{\partial}{\partial \tau}\left(\frac{P}{\tau}\right) = \frac{1}{R}\frac{\partial R}{\partial \tau},$$

and

$$\frac{1}{\frac{S_R'}{\tau}} \frac{\partial}{\partial \tau}\left(\frac{S_R'}{\tau}\right) = \frac{1}{Q_N'}\frac{\partial Q_N'}{\partial \tau}.$$

Integration gives at once:

$$\frac{P}{\tau} = \text{const}_1 R,$$

and

$$\frac{S_R'}{\tau} = \text{const}_2 Q_N'.$$

The constants are independent of temperature, but may of course vary from substance to substance.

Furthermore, $Q_N' = P/\tau$, as was shown in the preceding paper to be demanded by the energy relations. We therefore have the relations:

$$R = \text{const}_3 \frac{P}{\tau} = \text{const}_3 Q_N' = \text{const}_4 \frac{S_R'}{\tau} \cdot \tag{10}$$

That is, R, P/τ, Q_N', and S_R'/τ all depend on temperature in the same way, and therefore, in particular, all vanish in the same way at 0°K.

In addition to the relation $P/\tau = Q_N'$ deduced in the previous paper from the first law of thermodynamics, two other relations were also deduced from much more doubtful premises, such, for example, as the assumption that the rotation of the equipotential lines is the fundamental feature of the Hall effect, and is the same whether the potential drop is an iR drop as in an ordinary conductor, or whether it somes from a Thomson effect in an unequally heated bar. These two other relations were: $Q_N' = \sigma/k\rho R$, and $P = \sigma\tau S_R'$, where σ is the Thomson coefficient and ρ specific electrical resistance. Consistency of these relations with those above would demand that $\sigma/k\rho = \text{const}$, and $\sigma = \text{const}/\tau$. But $1/k\rho$ is the Wiedemann-Franz ratio, and varies approximately inversely as τ, so that the first relation demands that σ vary directly as τ, while the second demands that it be inversely proportional to τ. One or both of the previous relations must be given up. It is probable that neither is exactly correct, because the experimental evidence would not seem to indicate that σ varies either directly or inversely as τ in general. Of the two relations, the first, $Q_N' = (\sigma/k\rho)R$, rests on the more questionable argument and seems definitely not to agree with experiment in the case of metallic Co. At the time of writing that paper the relation was apparently satisfied for Co, using the value of Moreau[3] for the Nernst coefficient, Q_N'. Professor E. H. Hall, however, was of the opinion that the sign of Moreau's Q_N' was incorrect and checked this opinion by a redetermination of Q_N' experimentally. The only way of saving the relation was therefore by assuming that the usual sign of σ for Co is incorrect. I made a redetermination of σ on two pieces of Co cut longitudinally and transversely from the same specimen as used by Professor Hall, and verified that σ has the accepted sign. These measurements have not been previously reported. According to the best experimental evidence, therefore, the relation definitely fails for Co, and of course cannot be regarded as a general relation. It is still noteworthy, however, that the rela-

[3] G. Moreau, discussed on page 227 of the book by L. L. Campbell, Galvanomagnetic and Thermomagnetic Effects, Longmans, 1923. The numerical values and notation of this paper are taken from Campbell's book.

tion is satisfied by most other metals within experimental error, which must be admitted to be large.

At present I can see no argument of a plausible character suggesting another relation to replace $Q_N'=(\sigma/k\rho)R$. The second relation, however, $P=\sigma\tau S_R'$, may be replaced by another very similar to it with much plausibility. In a paper on conclusions to be drawn from the existence of various thermo-electric phenomena in crystals[4] I showed that the electric current I, must be recognized to convect with it a thermal current of magnitude $I\tau\int_0^\tau \sigma d\tau/\tau$. In particular, the longitudinal electric current of the Hall effect convects with it this amount of thermal energy. This heat flow will give rise to a transverse temperature gradient by the Righi-Leduc effect. If we make the simple assumption that this is the entire transverse temperature gradient when the longitudinal electric current flows, we have at once a connection between the Ettingshausen and the Righi-Leduc coefficients, namely:

$$P = \tau S_R' \int_0^\tau \frac{\sigma d\tau}{\tau},$$

which differs from the relation previously proposed only in that σ is replaced by $\int_0^\tau \sigma d\tau/\tau$. One would expect these two quantities to be of approximately the same magnitude; examination of the experimental evidence will show that the experimental accuracy is not great enough to give much significance to apparent differences, and that the new relation may be considered to be verified by experiment with the same degree of accuracy as the old relation. Consistency of the new relation with Eq. (10) demands that $\tau\int_0^\tau \sigma d\tau/\tau$ be constant, which gives on integration, $\sigma=\text{const}/\tau$. This cannot be a rigorously correct relation, because, among other things, it would give an infinite value to the integral at the lower limit, and therefore an infinite thermal energy convected by the electric current. The Ettingshausen temperature gradient cannot, therefore, all originate in the simple way suggested, but a large part of it must be of this origin, as shown by the approximate experimental check of the relation between P and S_R'.

Finally, we try to form an idea of the magnitude of the small effects neglected in the argument above. There is in the first place a heating effect associated with a change in the current. Imagine a closed electric circuit carrying a current i, in which the current is maintained by the self induction L, and in which the Joulean dissipation may be neglected. This system is determined thermodynamically by its temperature τ and the current i, and these may be taken as the independent variables fixing the state of the system. Temperature may be varied by any conventional means; i may be varied by inserting into the circuit an e.m.f. ϵ through which the system delivers or receives work from the outside, with accompanying change of i. The rate at which work is exchanged with the surroundings is, under these conditions:

$$\frac{dw}{dt} = \epsilon i.$$

[4] P. W. Bridgman, Phys. Rev. **31**, 221–235 (1928).

The change of i during the action of ϵ is governed by the ordinary equation of balance of e.m.f.'s, which in this case gives the statement that ϵ is balanced by the e.m.f. of self induction and the temperature e.m.f. already discussed. This gives:

$$L\frac{di}{dt} + iL\frac{1}{R}\frac{dR}{d\tau}\frac{d\tau}{dt} = \epsilon.$$

The first law of thermodynamics gives:

$$dQ = dW + dE,$$

where E is the internal energy, or,

$$dQ = \epsilon i dt + dE.$$

Put $dE = \partial E/\partial\tau d\tau + \partial E/\partial i di$, and substitute the value for ϵ, obtaining,

$$dQ = \left(\frac{\partial E}{\partial\tau} + i^2L\frac{1}{R}\frac{dR}{\partial\tau}\right)d\tau + \left(\frac{\partial E}{\partial i} + iL\right)di.$$

Form dS by dividing by τ, and formulate the condition that this be a perfect differential as usual by equating the cross derivatives. This gives at once:

$$\left(\frac{\partial Q}{\partial i}\right)_\tau = -2\tau iL\frac{1}{R}\frac{dR}{d\tau}\cdot$$

This gives the inflow of heat required to maintain the system isothermal when the current is altered. By dividing by the heat capacity we can at once obtain the approximate change of temperature when the current is altered adiabatically. For ordinary circuits such temperature effects are very small. Thus, in a toroid of bismuth of 10 cm radius and 1 cm thickness, the change of temperature when current is increased from 0 to 100 amp/cm^2 is of the order of 10^{-13} degrees centigrade.

The story is not completely told by these considerations. To characterize completely the system it would be necessary to determine the internal energy as a function of temperature and current. It may be shown by considerations which need not be given in detail here that the internal energy is not merely additive of the ordinary electrodynamic energy $\frac{1}{2}Li^2$ and the ordinary thermal energy when there is no current, but there must be cross terms. This means that the specific heat depends on the current. The precise influence of the current on the specific heat is not determined by the phenomena hitherto discussed, but apparently involves a new constant of the substance, which must be determined by independent experiment. We may attempt an estimate of the order of magnitude as follows. We have already seen that a current convects with it a thermal energy $\tau\int_0^\tau \sigma d\tau/\tau$; a good enough approximation for our purpose to this somewhat complicated expression is $\tau\sigma$. In the metal cobalt σ is unusually large, being 2.2×10^{-6} volts/°C. This means that one coulomb convects with it the thermal energy $(273\times2.2\times10^{-6})/4.2 = 1.4\times10^{-4}$

gm cal., which means that when the current density is 1 amp./cm^2, 1.4×10^{-4} gm cal. of thermal energy is convected across each square centimeter in one second. This energy flow is to be thought of as having a velocity and therefore a space density, and it is in virtue of the space density that the specific heat of a conductor carrying a current is different from that of the conductor without the current. Both the velocity and the corresponding space density are entirely unknown. Perhaps the most immediate assumption is that the velocity is the same as that of the electrons which constitute the current. This may be computed by assuming, as in the Sommerfeld theory, that the number of conduction electrons is the same as the number of atoms. This gives a velocity of 6×10^{-5} cm/sec for Co, which means a density of energy of $1.4\times10^{-4}/6\times10^{-5}=2$ gm cal./cm^3. So large a value appears inadmissible, since it would demand measureable effects on the specific heat, and would also demand that the apparent self induction of a circuit be appreciably dependent on the temperature as well as on the geometrical dimensions. If, on the other hand, the proper velocity to be associated with the convected thermal energy is the velocity of sound propagation, as it is for an ordinary thermal current, the effects will be smaller by a factor of 10^{11}, and therefore beyond experimental reach.

A corresponding analysis may be carried through for thermal flow, but the corresponding effects are more difficult to visualize because of the absence of a thermal self induction. If however, the space density of energy associated with the thermal current is taken as the analogue of the energy of self induction, corresponding results may be found. It will be found that there is a "thermo-motive" force in a body carrying a thermal current when the temperature changes. Analysis like that for the electrical case gives a simpler result because the energy associated with the thermal current is to be taken as proportional to the thermal current, rather than proportional to the square, as in the electrical case. This will lead to a heating effect in a substance in which the thermal conduction current is altered, which turns out to be proportional to the absolute temperature. But all this is so far beyond the reach of experiment that it is of little profit to pursue the matter further. It is, however, perhaps of interest to attempt to form an idea of the order of magnitude of the space density of energy associated with a thermal current. Imagine a centimeter cube of copper between the opposite faces of which there is a temperature difference of 100°. The thermal flux is approximately 100 cal./sec. The volume density of energy corresponding to this flux is such that its product into the velocity of flux is equal to 100. For the velocity we may take, in accordance with the Debye picture of thermal conduction, the velocity of sound, which for copper is about 3.5×10^6 cm/sec. The space density of energy is therefore $100/3.5\times10^6=3\times10^{-5}$ gm cal./cm^3. The heat capacity of 1 cm^3 of copper is about 0.8 gm cal. This means, therefore, that if a copper cube in which a thermal current of 100 cal./sec is flowing is suddenly isolated from the source and sink of heat flow, its final equilibrium temperature will be about 4×10^{-5} °C higher than its average temperature during the flow.

This, of course, would be very difficult to detect. It is interesting, however, that if a different velocity were assumed, as for example a velocity of the order of a few cm per sec., which is the order of the apparent velocity with which the maxima or minima of ordinary periodic thermal disturbances sink into the metal, a temperature effect of the order of many degrees would have been found. This affords rather direct confirmation of the correctness of the Debye point of view. The experiment might be worth making to find how far the velocity limit could be pushed.