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KINETIC INTERPRETATION OF THE KELVIN RELATIONS

By E. A. Uehling
Department of Physics, University of Michigan

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Abstract

The derivation of the Kelvin relations for the reversible heat development and the thermo-electric force in crystals is shown to depend only on the assumption of the principle of detailed balancing. Previous treatments of this subject have been less general. The work of Nordheim is valid only for isotropic materials, and that of Ehrenfest and Rutgers, though applicable to crystals, depends on the assumption of elastic collisions between the electrons and the atoms of the metal. In both treatments the electrons are assumed to be completely free and to be described by an energy function which is spherically symmetrical. All of these restricting assumptions are removed. The solution of the integral equation describing the distribution function of the electrons is obtained by a general method which depends only on the assumption of detailed balancing. This principle gives the integral equation an essentially symmetrical kernel, as a consequence of which a formal solution may be obtained. One may use this solution to derive the electric and heat current equations and to prove certain reciprocal relations from which the Kelvin equations follow. The proof of the existence of these relations, involving as it does only the assumption of detailed balancing, may be considered as a substantiation for the case of conduction in metals of certain very general considerations of Onsager.

§1. Introduction

A KINETIC derivation of the Kelvin relations for the reversible heat development and the thermo electric-force in metals has been given by Nordheim[1] for isotropic materials and by Ehrenfest and Rutgers[2] for crystals. In addition to the principle of detailed balancing which plays an essential role in all kinetic interpretations the following assumptions have been used: (a) Both treatments make use of an energy function which in terms of wave numbers or of the electron velocities is spherically symmetrical. This is equivalent to the assumption that the electrons are completely free. (b) Nordheim makes assumptions that restrict the application of his conclusions to isotropic materials. (c) Ehrenfest and Rutgers consider crystals as well as isotropic materials, but they introduce the restricting assumption of elastic collisions between the electrons and the ions of the crystal lattice. Both treatments are entirely general with respect to statistics.[3]

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[1] L. Nordheim, Ann. d. Physik, [5], 9, 607 (1931). Zur Elektronentheorie der Metalle. I, II.

[2] P. Ehrenfest und A. J. Rutgers, Proc. Kon. Acad. Amst. **32**, 698, 883 (1929). Zur Thermodynamik und Kinetik der thermoelektrischen Erscheinungen in Krystallen, insbesondere des Bridgman-Effektes. II. A. J. Rutgers, Dissertation Leiden, 1930.

[3] Independence of statistics is obtained by using the function:

$$f_0 = g(Ae^{-\epsilon/KT}) \tag{1}$$

to describe the equilibrium distribution of the electron energies. In this equation ϵ is the total energy of an electron in a certain cell in momentum space, f_0 represents the number of electrons

The author proposes to show that the restricting assumptions a, b, and c are unnecessary, and that *a derivation of the current equations and the Kelvin relations can be given when one retains only the principle of detailed balancing.*

§2. THE ELECTRIC AND HEAT CURRENT EQUATIONS

Using the special assumptions described, Nordheim obtains the following equations for the electric and heat currents in an isotropic material:

$$i_x = eK_1\left(eF_x - \frac{KT}{A}\frac{\partial A}{\partial x}\right) - \frac{eK_2}{T}\frac{\partial T}{\partial x} \tag{2}$$

$$w_x = K_3\left(eF_x - \frac{KT}{A}\frac{\partial A}{\partial x}\right) - \frac{K_4}{T}\frac{\partial T}{\partial x} \tag{3}$$

where F_x is the electric field, $\partial T/\partial x$ is the temperature gradient, K is the Boltzmann constant, and A is the coefficient in the distribution function (1). The four coefficients, K_1, K_2, K_3 and K_4 are functions of the temperature and the coordinates, and they depend, furthermore, upon a function which describes the behavior of the electrons in collisions, and upon the choice of statistics. Among these coefficients Nordheim finds the important *reciprocal relation*

$$K_2 = K_3. \tag{4}$$

The validity of the Kelvin relations is shown to depend upon the existence of this condition.

Ehrenfest and Rutgers, using the special assumptions described, obtain the following equations for the electric and heat conduction currents in anisotropic crystals:

$$i_s(x_1x_2x_3) = eK_{rs}^{(1)}\left[eF_r - \frac{KT}{A}\frac{\partial A}{\partial x_r}\right] - \frac{eK_{rs}^{(2)}}{T}\frac{\partial T}{\partial x_r} \tag{5}$$

$$w_q(x_1x_2x_3) = eK_{rq}^{(2)}\left[eF_r - \frac{KT}{A}\frac{\partial A}{\partial x_r}\right] - \frac{K_{rq}^{(3)}}{T}\frac{\partial T}{\partial x_r} \tag{6}$$

where the appearance of a letter twice as an index in a single term indicates a summation for that letter over the numbers 1, 2, and 3. The three coefficients are symmetrical tensors which are functions of position and temperature, and which depend, furthermore, upon the nature of the function which describes electron transitions in collision, and upon the choice of statistics. The *reciprocal relation* existing between the two current equations is in this case the appearance of the same coefficient $K_{rp}^{(2)}$ in both equations. Since it is symmetrical

$$K_{rp}^{(2)} = K_{pr}^{(2)}. \tag{7}$$

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in such a cell, T is the absolute temperature, K is the Boltzmann constant, and A is a coefficient depending on temperature and position, which is determined by setting the sum of f_0 over all cells of momentum space equal to the total number of electrons. The form of the function g depends on the choice of statistics.

This condition is essential in the derivation of the Kelvin relations from the current equations.

Assuming only the principle of detailed balancing one obtains the following equations for the electric and heat currents in crystals:

$$i_s(x_1x_2x_3) = eK_{rs}^{(1)}\left[eF_r - \frac{KT}{A}\frac{\partial A}{\partial x_r}\right] - \frac{eK_{rs}^{(2)}}{T}\frac{\partial T}{\partial x_r} \tag{8}$$

$$w_q(x_1x_2x_3) = K_{rq}^{(3)}\left[eF_r - \frac{KT}{A}\frac{\partial A}{\partial x_r}\right] - \frac{K_{rq}^{(4)}}{T}\frac{\partial T}{\partial x_r}\,. \tag{9}$$

These equations differ from those of Ehrenfest and Rutgers in the meaning of the tensor coefficients and in the existence of four such functions instead of three. Unlike the tensors $K_{rp}^{(2)}$ of Ehrenfest and Rutgers, *the coefficients* $K_{rs}^{(2)}$ *and* $K_{rq}^{(3)}$ *are not, in general, symmetrical in their indices.*[4] Nevertheless, one may show that under all conditions the reciprocal relation:

$$K_{rq}^{(2)} = K_{qr}^{(3)} \tag{10}$$

exists between these equations. The other two coefficients $K_{rs}^{(1)}$ and $K_{rq}^{(4)}$ are always symmetrical in their indices. These conditions are just sufficient for the derivation of the Kelvin relations.[5]

Conditions (4), (7) and (10), which have been found to exist in the three different treatments of this subject, are special cases of a general class of such relations. Onsager,[6] who has considered irreversible phenomena in general, finds that one may demonstrate the existence of reciprocal relations of this kind between any two processes which are not independent if the principle of detailed balancing is assumed. The conclusions described above may be taken as a substantiation for the case of conduction in metals of these more general and rather abstract considerations.

§3. General Method

The foundation of these derivations is the well-known Boltzmann equation for the distribution function f of the electrons. This equation may be written in the form:

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[4] The explicit form of these tensors which is to be given later shows that they are symmetrical in their indices only when the function representing the total energy of the electron is separable in three terms, each of which depends on a single quantum number and is the same function of its argument as each of the other two; i.e., the energy must be of the form:

$$\epsilon = f(k_1) + f(k_2) + f(k_3).$$

Since it may rarely, if ever, be possible to express the energy for any actual metal in this form, the coefficients $K_{rs}^{(2)}$ and $K_{rq}^{(3)}$ of the current equations are not, in general, symmetrical.

[5] Since the current equations have been derived under the single assumption of detailed balancing with all restricting assumptions removed, these relations may be considered as the necessary and sufficient conditions upon which the validity of the Kelvin relations is based. As is to be expected, these conditions are in general weaker than those found by Ehrenfest and Rutgers and by Nordheim.

[6] Lars Onsager, Phys. Rev. **37,** 405–426 (1931). Reciprocal Relations in Irreversible Processes. I.

$$X_r \frac{\partial f}{\partial \xi_r} + \xi_r \frac{\partial f}{\partial x_r} = \int\int\int w(P'P)f(P')[1+\theta f(P)]dk_1'dk_2'dk_3' - \int\int\int w(PP')f(P)[1+\theta f(P')]dk_1'dk_2'dk_3' \tag{11}$$

where X_r is the rth component of the acceleration of an electron, ξ_r is the rth component of the mean velocity of drift, $w(PP')$ is a function describing the transition probability of an electron in a cell P of momentum space to a cell P', k_r is the quantum wave number in the rth direction of space, and θ has the value 1, 0, or -1 depending on whether the choice of statistics is Einstein-Bose, Maxwell-Boltzmann, or Fermi-Dirac. Introducing the principle of detailed balancing:

$$f_0(P)[1+\theta f_0(P')]w(PP') = f_0(P')[1+\theta f_0(P)]w(P'P) \tag{12}$$

one obtains a relation between the probabilities of the direct process $(P \rightarrow P')$ and the restituting process $(P' \rightarrow P)$ which for all statistics is given by the equation:

$$w(PP')e^{\epsilon'/KT} = w(P'P)e^{\epsilon/KT} = W(PP') = W(P'P). \tag{13}$$

The new function $W(PP')$ defined by this equation is obviously symmetrical in all of the primed and unprimed variables on which it depends. Since no further assumptions have been made, it must be considered as a function of all the variables by which a cell in momentum space is specified and, in general, of the coordinates as well. Then it may be written as $W(x_1x_2x_3kk'a_1a_2a_3\text{-}a_1'a_2'a_3')$ where $x_1x_2x_3$ are the coordinates, k the absolute magnitude of the wave number, and $a_1a_2a_3$ the direction cosines of the electron velocity.[7] The introduction of this function into the Boltzmann equation eliminates the unsymmetrical probability function from the equation and gives the foundation for the further treatment which is to follow.

One attempts to solve this equation by writing:

$$f = f_0 + f_1 \tag{14}$$

where f_1 is a small perturbation term. Introducing Eqs. (13) and (14) into Eq. (11), neglecting second order terms, and writing x for $x_1x_2x_3$ and a for $a_1a_2a_3$ one obtains:

$$X_r \frac{\partial f_0}{\partial \xi_r} + \xi_r \frac{\partial f_0}{\partial x_r} = \int d\phi' W(xkk'aa')\left[\frac{f_0 f_1'}{f_0'} e^{-\epsilon'/KT} - \frac{f_0' f_1}{f_0} e^{-\epsilon/KT}\right] \tag{15}$$

where $d\phi' = dk_1'dk_2'dk_3'$. This equation is to be solved for the unknown perturbation function f_1. Various methods of accomplishing this result, which are possible when certain restricting assumptions are made, have been used

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[7] An essential difference in the three treatments exists at this point. Nordheim, considering isotropic materials, writes the probability function as $w(x_1x_2x_3kk'\theta)$ where θ is the angle between the vectors representing k and k'. Ehrenfest and Rutgers, considering crystals but assuming that all electron collisions are elastic, write w as $w(x_1x_2x_3v;\, a_1a_2a_3a_1'a_2'a_3')$.

in the previous theoretical treatments of conduction in metals.[8] When no such assumptions are made, a very general method of solution, according to which the unknown function is formally expressed in terms of a symmetrical solving function $S(xkk'aa')$ must be used. This method, like all others, depends essentially on the principle of detailed balancing, but, unlike these other methods, it requires no restricting assumptions of any kind.

§4. FORMAL SOLUTION OF THE INTEGRAL EQUATION; DETERMINATION OF THE ELECTRIC AND HEAT CURRENT EQUATIONS

The left member of the integral equation must be written in terms of wave numbers before a solution can be obtained. The foundation of this transformation is the Peierls theorem[9] which relates the mean velocity of drift of an electron through a crystal lattice to the differential quotient of its total energy with respect to the wave number:

$$\xi_r = \frac{L}{h}\frac{\partial \epsilon}{\partial k_r} \tag{16}$$

where L is the length of the crystal, and h is Planck's constant. Using this theorem one obtains for electrons of any degree of binding subjected to an external electric field of components F_r, ($r = 1$, 2, and 3).

$$X_r = eF_r \frac{L}{h}\frac{\partial \xi_r}{\partial k_r} \tag{17}$$

$$\frac{\partial f_0}{\partial \xi_r} = \frac{h}{L}\xi_r \frac{\partial f_0}{\partial \epsilon} \bigg/ \frac{\partial \xi_r}{\partial k_r} \tag{18}$$

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[8] Nordheim, using a method of solution introduced by Lorentz, writes f_1 as the product of two functions:

$$f_1 = k \cos \theta \chi(k) = k_x \chi(k)$$

where k is the absolute magnitude of the wave number, and θ is the angle between the direction of the electron velocity and the direction of the potential and temperature gradients. The equation in f_1 is reduced in this manner to an equation in $\chi(k)$ which may be solved by general methods. The assumption that f_1 is a function of this form is easily justified when the fundamental equation is descriptive of processes in isotropic media, but not otherwise, for it is only in such materials that the heat and electric currents can be assumed to have the same direction as the temperature and potential gradients. Ehrenfest and Rutgers obtain a solution in the anisotropic case by writing the perturbation function as

$$f_1 = P_r(xv) \cdot G_r(xv;\, a_1a_2a_3)$$

where $P_r(xv)$ is the coefficient of a_r in the left member of the Boltzmann equation, and the functions $G_r(xv;\, a_1a_2a_3)$, where r has the values 1, 2, and 3, are the solutions of the three integral equations into which the original one is decomposed. This method of solution is possible only when the absolute magnitude of the electron velocity v, or its corresponding wave number k, is not one of the integration variables. It cannot be used, therefore, when the assumptions of Ehrenfest and Rutgers are not made.

[9] This theorem has been proved by R. Peierls (Zeits. f. Physik **53**, 255 (1929), Zur Theorie der galvanomagnetischen Effekte) for nearly free electrons. It is valid, however, for electrons of all degrees of binding. A general proof of the theorem has been received from J. R. Oppenheimer in a communication by letter to G. E. Uhlenbeck.

$$X_r \frac{\partial f_0}{\partial \xi_r} = eF_r \xi_r \frac{\partial f_0}{\partial \epsilon} \tag{19}$$

Also

$$\frac{\partial f_0}{\partial x_r} = -\frac{\partial f_0}{\partial \epsilon}\left[\frac{KT}{A}\frac{\partial A}{\partial x_r} + \frac{\epsilon}{T}\frac{\partial T}{\partial x_r}\right] \tag{20}$$

for all statistics. Then the left member of the integral equation becomes:

$$\xi_r \frac{\partial f_0}{\partial \epsilon}\left[eF_r - \frac{KT}{A}\frac{\partial A}{\partial x_r} - \frac{\epsilon}{T}\frac{\partial T}{\partial x_r}\right] \tag{21}$$

$$= u_r \frac{\partial f_0}{\partial \epsilon}[P_r(x_1x_2x_3) + \epsilon Q_r(x_1x_2x_3)] \tag{22}$$

where

$$P_r(x_1x_2x_3) = eF_r - \frac{KT}{A}\frac{\partial A}{\partial x_r} \tag{23}$$

$$Q_r(x_1x_2x_3) = -\frac{1}{T}\frac{\partial T}{\partial x_r} \tag{24}$$

and u_r is the mean velocity of drift considered as a completely arbitrary function of all the quantum numbers.

Now define a new function g_1 by means of the equation

$$f_1 = -\frac{\partial f_0}{\partial \epsilon} g_1 = \frac{f_0^2}{AKT} e^{\epsilon/KT} g_1. \tag{25}$$

Introducing this function into the integral Eq. (15), using expression (22) for the left member, and multiplying both members by k^2, one obtains

$$\begin{aligned} &f_0^2 e^{\epsilon/KT} k^2 u_r [P_r(x) + \epsilon Q_r(x)] \\ &= g_1 \int_{k'} k^2 k'^2 dk' \int_{w'} d\omega' W(xkk'aa') f_0 f_0 \\ &\quad - \int_{k'} k^2 k'^2 dk' \int_{w'} d\omega' W(xkk'aa') g_1' f_0 f_0'. \end{aligned} \tag{26}$$

The kernel of this integral equation is symmetrical in all primed and unprimed variables, since $W(xkk'aa')$ is symmetrical in these variables. Then a formal solution containing a symmetrical solving function may be obtained directly. This solution is:

$$\begin{aligned} g_1(xka) &= \frac{f_0^2 e^{\epsilon/KT} k^2 u_r P_r(x)}{H(ka)} + \frac{f_0^2 e^{\epsilon/KT} k^2 u_r \epsilon Q_r(x)}{H(ka)} \\ &\quad + \int dk' \int d\omega' \frac{f_0'^2 e^{\epsilon'/KT} k'^2 u_r' P_r(x)}{(H(k'a')H(ka))^{1/2}} S(xkk'aa') \end{aligned} \tag{27}$$

$$+ \int dk' \int d\omega' \frac{f_0'^2 e^{\epsilon'/KT} k'^2 u_r' \epsilon' Q_r(x)}{(H(k'a')H(ka))^{1/2}} S(xkk'aa')$$

$$= P_r(x)G_r(xka) + \epsilon Q_r(x)J_r(xka) \tag{28}$$

where

$$G_r(xka) = \frac{f_0^2 e^{\epsilon/KT} k^2 u_r}{H(ka)} + \int dk' \int dw' \frac{f_0'^2 e^{\epsilon'/KT} k'^2 u_r'}{(H(k'a')H(ka))^{1/2}} S(xkk'aa') \tag{29}$$

$$J_r(xka) = \frac{f_0^2 e^{\epsilon/KT} k^2 u_r}{H(ka)} + \int dk' \int dw' \frac{f_0'^2 e^{\epsilon'/KT} k'^2 u_r'}{(H(k'a')H(ka))^{1/2}} \frac{\epsilon'}{\epsilon} S(xkk'aa')$$

$$H(xka) = \int k^2 k'^2 dk' \int d\omega' W(xkk'aa') f_0 f_0' \tag{31}$$

and $S(xkk'aa')$ is the symmetrical solving function.

The first order perturbation term f_1 is obtained from this expression for g_1, and the electron and heat current equations are obtained by introducing this expression for f_1 into the equations:

$$i_s = \frac{Ge}{L^3} \int\int\int u_s f_1 dk_1 dk_2 dk_3 \tag{32}$$

$$w_q = \frac{G}{L^3} \int\int\int u_q \epsilon f_1 dk_1 dk_2 dk_3. \tag{33}$$

One obtains:

$$f_1 = -\frac{\partial f_0}{\partial \epsilon} \{ P_r(x)G_r(xka) + \epsilon Q_r(x)J_r(xka) \} \tag{34}$$

$$i_s(x_1x_2x_3) = -\frac{Ge}{L^3} \int k^2 P_r(x)\Gamma_{rs}(xk)dk - \frac{Ge}{L^3} \int k^2 Q_r(x)\Lambda_{rs}(xk)dk \tag{35}$$

$$w_q(x_1x_2x_3) = -\frac{G}{L^3} \int k^2 P_r(x)\Pi_{rq}(xk)dk - \frac{G}{L^3} \int k^2 Q_r(x)\Delta_{rq}(xk)dk \tag{36}$$

where

$$\Gamma_{rq}(xk) = \int d\omega u_q \frac{\partial f_0}{\partial \epsilon} G_r \tag{37}$$

$$\Lambda_{rq}(xk) = \int d\omega u_q \frac{\partial f_0}{\partial \epsilon} \epsilon J_r \tag{38}$$

$$\Pi_{rq}(xk) = \int d\omega u_q \frac{\partial f_0}{\partial \epsilon} \epsilon G_r \tag{39}$$

$$\Delta_{rq}(xk) = \int d\omega u_q \frac{\partial f_0}{\partial \epsilon} \epsilon^2 J_r \tag{40}$$

and G is the weight attributed to an energy level. These equations are equivalent to (8) and (9) where

$$K_{rq}^{(1)} = -\frac{G}{L^3}\int k^2\Gamma_{rq}(xk)dk \tag{41}$$

$$K_{rq}^{(2)} = -\frac{G}{L^3}\int k^2\Lambda_{rq}(xk)dk \tag{42}$$

$$K_{rq}^{(3)} = -\frac{G}{L^3}\int k^2\Pi_{rq}(xk)dk \tag{43}$$

$$K_{rq}^{(4)} = -\frac{G}{L^3}\int k^2\Delta_{rq}(xk)dk. \tag{44}$$

Introducing the values of G_r and J_r from (29) and (30) into the four tensors Γ, Λ, Π and Δ one finds readily that the coefficients $K_{rq}^{(2)}$ and $K_{rq}^{(3)}$ are not symmetrical in their indices unless the conditions described in note 4 are fulfilled. Therefore these coefficients are, in general, unsymmetrical. But the reciprocal relation

$$K_{rq}^{(2)} = K_{qr}^{(3)} \tag{10}$$

does exist, for

$$\begin{aligned} K_{rq}^{(2)} = & -\frac{G}{L^3}\int k^2dk \int d\omega \frac{\partial f_0}{\partial \epsilon} u_q u_r \epsilon \frac{f_0{}^2 e^{\epsilon/KT} k^2}{H(ka)} \\ & -\frac{G}{L^3}\int dk \int d\omega \int dk' \int d\omega' k^2 k'^2 u_q u_r' \\ & \cdot\frac{\partial f_0}{\partial \epsilon} \frac{f_0'^2 e^{\epsilon'/KT}\epsilon'}{(H(k'a')H(ka))^{1/2}} S(xkk'aa') \end{aligned} \tag{45}$$

$$\begin{aligned} K_{qr}^{(3)} = & -\frac{G}{L^3}\int k^2dk \int d\omega \frac{\partial f_0}{\partial \epsilon} u_r u_q \epsilon \frac{f_0{}^2 e^{\epsilon/KT} k^2}{H(ka)} \\ & -\frac{G}{L^3}\int dk \int d\omega \int dk' \int d\omega' k^2 k'^2 u_r u_q' \\ & \cdot\frac{\partial f_0}{\partial \epsilon} \frac{f_0'^2 e^{\epsilon'/KT}\epsilon}{(H(k'a')H(ka))^{1/2}} S(xkk'aa'). \end{aligned} \tag{46}$$

Since $S(xkk'aa')$ and $(H(k'a')H(ka)^{1/2}$ are symmetrical in primed and unprimed variables, and

$$\frac{\partial f_0}{\partial \epsilon} = -\frac{f_0{}^2}{AKT} e^{\epsilon/KT}$$

these expressions are equal, for primed and unprimed quantities may be interchanged in the second term of either expression without changing its value.

5. THE KELVIN EQUATIONS

Following Ehrenfest and Rutgers one may write the current equations in the form

$$i_s = A_{rs} e F_r + B_s \tag{47}$$

$$w_q = C_{rq} e F_r + D_q \tag{48}$$

where

$$A_{rs} = eK_{rs}^{(1)} \tag{49}$$

$$B_s = -\, eK_{rs}^{(1)} \frac{KT}{A} \frac{\partial A}{\partial x_r} - \frac{eK_{rs}^{(2)}}{T} \frac{\partial T}{\partial x_r} \tag{50}$$

$$C_{rq} = K_{rq}^{(3)} \tag{51}$$

$$D_q = -K_{rq}^{(3)} \frac{KT}{A} \frac{\partial A}{\partial x_r} - \frac{K_{rq}^{(4)}}{T} \frac{\partial T}{\partial x_r}\,. \tag{52}$$

The Kelvin relations for the reversible heat development and the thermo-electric force are obtained from these equations and a third equation giving the total heat development Ω:

$$\Omega = F_q i_q - \frac{\partial w_p}{\partial x_p}\,. \tag{53}$$

One obtains for the reversible part χ of the total heat developed the expression

$$\chi = -\, i_q B_s \frac{a_{qs}}{e} - \frac{\partial}{\partial x_p}(a_{qs} i_s C_{qp}) \tag{54}$$

and for the thermo-electric force F_q:

$$F_q = -\frac{B_s}{e} a_{qs} \tag{55}$$

where a_{qs} is a tensor which is the reciprocal of the tensor $eK_{qs}{}^{(1)}$ and is defined by the equation:

$$a_{qs} K_{rs}^{(1)} = \frac{\delta_{qr}}{e}\,. \tag{56}$$

The coefficients $K_{qs}{}^{(1)}$ and $K_{qs}{}^{(4)}$ unlike the coefficients $K_{qs}{}^{(2)}$ and $K_{qs}{}^{(3)}$ are always symmetrical. Therefore

$$a_{qs} = a_{sq}\,. \tag{57}$$

Introducing the expression for B_s, the general reciprocal relation (10), and Eq. (57) into Eqs. (54) and (55), one obtains the Kelvin equations:

$$\frac{\chi(x_1 x_2 x_3)}{T} = \frac{\partial}{\partial x_p}(i_s S_{sp}) \tag{58}$$

$$F_s = \frac{\partial R}{\partial x_s} - S_{ps} \frac{\partial T}{\partial x_p} \tag{59}$$

where

$$S_{sp} = K\left(\frac{S_{sp}}{e} \log A - a_{qs} K^{(3)}_{qp} \frac{1}{KT}\right) \tag{60}$$

$$R = \frac{KT}{e} \log A \,. \tag{61}$$

These equations are equivalent to those originally obtained by Lord Kelvin on the basis of thermo-dynamic reasoning. They have now been derived kinetically using only the assumption of detailed balancing. The essential role of this principle has been to provide the necessary symmetry in the integral equation which describes the distribution function of the electrons, on the basis of which a solution, also having certain essential symmetry characteristics, is possible. These characteristics have served to establish the symmetry of the tensor a_{qs} and the existence of important reciprocal relations between the current equations. The Kelvin relations depend essentially on these conditions.

I wish to express my gratitude to Professor G. E. Uhlenbeck for suggesting this problem.

Note added for correction: The index r of equations (17), (18), and (19) is not a dummy index. These developments are not strictly true unless the energy is separable in three functions, which may be different, of the three quantum numbers individually.