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Irreversible Thermodynamics of Thermoelectricity*

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INTRODUCTION. BASIC PROBLEM OF THERMOELECTRICITY

THE basic problem of thermoelectricity is the following: *Given a system consisting of one or several chemical phases and having a specified temperature distribution, it is required to determine the electronic electrochemical potential at any and all points within the system as well as at points in the immediate surroundings of the system.* We consider the electrochemical potential determination in the general sense of deducing this parameter from the over-all electronic and crystalline structure of the phases constituting the system; however, in this Review we shall treat only the thermodynamic aspects of the problem. We include in the problem the situation in the space immediately surrounding the actual material phases of the system in order to bring out the significance of the Volta potential difference. There seems to be some confusion with regard to the question of what relationship there is, if any, between the Volta potential difference and thermoelectricity. For this reason we have treated in Appendix B the subject of Volta potential differences.

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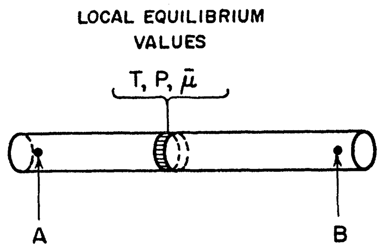

FIG. 1. Cylindrical rod of a single homogeneous chemical phase carrying steady-state electrical and heat currents; the thermostatic parameters vary from point to point.

The thermodynamic theory of thermoelectrical phenomena in isotropic media was first worked out by H. B. Callen[1] using the Onsager-Casimir methods, and is presented in more detail in de Groot's monograph.[2] The theory brings out very clearly the important role played in thermoelectricity by certain "transport" or "transfer" quantities which are strictly thermodynamical in nature and cannot be deduced from the thermostatic characteristics and parameters of a substance. We shall see that the thermoelectrically important parameters such as thermoelectric power are related in part to these transport quantities and in part to certain essentially thermostatic quantities, so that under certain conditions the thermoelectric properties of some substances can be treated quite properly in terms of the ordinary thermostatic characteristics of these substances, the transport contribution being negligible or nearly so. Now just as thermostatics leads to relations between the various thermostatic parameters of a phase without being able to derive values of these parameters from the general structural and atomic properties of the phase, so does thermodynamics relate the various transport parameters with each other without being able to derive actual values of these transport parameters from structural and atomic properties of the substance. Quantum-mechanical and statistical-mechanical calculations lead to actual numerical values for certain static parameters such as specific heats, for example, and from such information thermostatical methods are used to calculate almost all other static quantities of interest. Likewise, quantum mechanics and kinetic theory can lead to actual numerical values for certain dynamic or transport quantities such as the "heat of transfer" already mentioned, for example, and from such information thermodynamic methods are used to calculate other dynamic parameters of interest. The writer hopes that a review of the thermodynamics of thermoelectricity will stimulate among theoretical physicists an interest in the quantum theoretical calculation of these pertinent transfer or transport parameters, both for metals and for semiconductors.

Finally, it should be mentioned that there are still conceptual difficulties in the Onsager theory, not the least important of which has to do with the laws of decay or regression of fluctuations. Furthermore, the theory is strictly *linear* or what might be called a "first approximation" transport theory. (In this connection see Sec. I of this Review, on the Benedicks effects.) For discussions of these more abstruse questions the reader must refer to the original literature.[1,2]

A. ELECTROCHEMICAL POTENTIAL: ITS SEPARATION INTO CHEMICAL AND ELECTRICAL PARTS

The electrochemical potential $\bar{\mu}_i^\beta$ of the component i (an ion, a hole, or an electron) in an isotropic, homogeneous, chemical phase β is defined for a system in thermostatic equilibrium as

$$\bar{\mu}_i^\beta \equiv \left(\frac{\partial G}{\partial N_i}\right)_{P,T} \equiv \left(\frac{\partial H}{\partial N_i}\right)_{S,P} \equiv \left(\frac{\partial A}{\partial N_i}\right)_{T,V} \equiv \left(\frac{\partial U}{\partial N_i}\right)_{S,V}. \tag{1}$$

Here the phase β is supposed to be a part of the complete system with total volume V and entropy S, and the temperature T and pressure P are assumed to be uniform throughout the entire system. The quantities G, H, A, and U are, respectively, the total Gibbs energy, the total enthalpy, the total Helmholtz energy, and the total internal energy of the entire system, and N_i is the number of the ith component contained in the system. If the system is not completely in thermostatic equilibrium and contains regions in which there exist gradients of temperature or flows of electrical charge or both, it is then not exactly obvious how one proceeds to define the electrochemical potential of the ith component in an arbitrary spot or region of the nonequilibrium system. For our purposes we simply assume that even in a nonequilibrium system the electrochemical potential of the ith component in phase β is in general a continuous and differentiable function of position and of temperature within the single homogeneous phase. We further assume the usual thermostatic condition of continuity of the electrochemical potential for component i in crossing the boundary between two phases in thermostatic equilibrium. In all situations with which we shall be concerned the electrochemical potential $\bar{\mu}_i^\beta$ is separable into a *chemical potential* μ_i^β (without bar) and an *electrical potential* ϕ^β in the form

$$\bar{\mu}_i^\beta = \mu_i^\beta + q\phi^\beta, \tag{2}$$

where q is the charge on the component i. Throughout this Review we shall always express energies in joules and charge in coulombs, and a table is given in Appendix F which gives the MKS units of all thermoelectric parameters of interest to us. From the defining relation (1) above we see that the electrochemical potential $\bar{\mu}_i^\beta$

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[1] H. B. Callen, Phys. Rev. **73**, 1349 (1948).

[2] S. R. de Groot, *Thermodynamics of Irreversible Processes* (Interscience Publishers, Inc., New York, 1951), Chapter VIII.

and the chemical potential $\mu_i{}^\beta$ are expressed in joules per particle $(\partial G/\partial N)$, which gives the product $q_i\phi^\beta$ in joules/particle. Therefore, expressing q_i in coulomb/particle we find that the electrical potential ϕ^β is in volts. The dissimilarity of units between quantities with the same label "potential" is regrettable; however, it seems best to use this very widely accepted terminology.

Our notation for potentials, while at first seeming to be unnecessarily cumbersome, is actually simple and has the important advantage of giving at a glance all the pertinent information about the potential, as follows. The symbol for an electrochemical potential is written $\bar{\mu}^{\text{phase (temp)}}_{\text{component}}$. The bar indicates an electrochemical potential; if the bar is missing the symbol refers to a chemical potential. The phase referred to is written as a first superscript, the second superscript (in parentheses) denoting the absolute temperature of the phase. The subscript following the symbol tells the component. The electrical *potential* in a given phase, indicated by the symbol $\phi^{\text{phase (temp)}}$, is independent of the nature of the component so that it is not necessary to add the component-subscript. On the other hand, for a component with charge q the electrical potential *energy* $q\phi^{\text{phase (temp)}}$ does depend on the component and this dependence is taken care of by the charge factor q. Thus the q subscript in $q\phi_q$ is superfluous. Finally, when all the potentials refer to the same temperature as in a completely thermostatic discussion, there is usually no need for the temperature superscript. Our notation is a combination and extension of those used by Guggenheim[3] and by de Groot.[2]

In order to illustrate the meaning of the separation into a chemical and an electrical part as indicated in (2) we consider in Appendix A the question of how one actually measures or otherwise determines numerical values of chemical and electrochemical potentials. It is clear that in all cases an arbitrary reference level for energies must be decided upon and that all chemical and electrochemical potentials must refer to such an arbitrary reference. For a given component the chemical portion $\mu_i{}^\beta$ can be looked upon as being determined by the chemical or atomic nature of the phase β, while the electrical portion $q_i\phi^\beta$ is determined by the distribution of electrical charges in the whole system as well as in the surroundings. The actual separation into a chemical and an electrical part in most practical cases is by no means easy and is quite often impossible. On the other hand, in some cases the separation can be made in a straightforward way.

B. PRINCIPLES OF STEADY-STATE THERMODYNAMICS

Consider a cylindrical rod consisting of a single homogeneous chemical phase, shown in Fig. 1. If the rod were in a state of thermostatic equilibrium all the thermostatic parameters would have uniform values throughout. In particular, there would be no temperature gradients and no gradients of the electronic electrochemical potential anywhere within the phase.[4] Next in complexity to thermostatic equilibrium is the situation called the *steady state*, and it is this state which we wish to study by means of the thermodynamic theory. The still more complicated problem, that involving transient conditions, can under certain conditions be treated with the general theory, but this does not interest us here.

For our purposes, a very general steady-state condition in the rod would consist of having a steady electrical current flowing along the rod together with a flow of heat along a longitudinal temperature gradient. Now while thermostatics and thermodynamics furnish general relations which are independent of any specific atomic or molecular models of matter, both theories are *statistical* in nature; and before either can be successfully applied to a given system it is necessary for the system to satisfy certain statistical requirements. In our case we must specify that if the rod in Fig. 1 has temperature gradients and electrical currents in it, these must be such that it is possible to define an electrochemical potential at all points in the rod. This is equivalent to saying that we must be able to assign values to all the usual thermostatic parameters at any point in the system. If the temperature gradients are so large, for example, that the fractional change in absolute temperature is not extremely small compared to unity when we go about a mean-free-path length along the rod, then it will be practically meaningless to assign values to thermostatic parameters along the rod.[5]

We shall assume, then, that for all systems of interest to us it is possible in principle to assign a value[6] to the electronic electrochemical potential at all points within and outside the various phases in the system. The problem is to relate the electrochemical potential distribution with the electrical current and temperature distribution in the system, and it is just this kind of problem which is solved by the Callen-de Groot method of applying the general thermodynamic theory of Onsager and Casimir.

The thermodynamic theory establishes *linear* relations between certain "flows" and the generalized "driving forces" which cause these flows. Special cases of such relations are the ordinary Ohm's law, which says that electrical current (flow) in an isothermal wire is proportional to the gradient of the electrical potential in the wire, the proportionality coefficient being the iso-

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[3] E. A. Guggenheim, *Thermodynamics, An Advanced Treatment* (Interscience Publishers, Inc., New York, 1951).

[4] Although the general thermodynamic theory (de Groot, reference 2, Chapters VII and VIII) is applicable to any and all carriers of electric charge inside a phase, electrons and ions alike, for definiteness we shall refer throughout this Review to the *electron*, with charge $-e$ (e positive), and the subscript $-e$ on the potentials will be left off unless required for clarity.

[5] C. Herring and M. H. Nichols, Revs. Modern Phys. **21**, 185 (1949).

[6] Referred of course to an arbitrary reference level.

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

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

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

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

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

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

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

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

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

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

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

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

$$\mathbf{Q}\equiv\mathbf{W}-\bar{\mu}\mathbf{J}_e. \tag{5}$$

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

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

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

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

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

$$\mathbf{J}_q=\mu\mathbf{J}_e+T\mathbf{J}_s. \tag{8}$$

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

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

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

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

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

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

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

$$(\nabla\bar{\mu}+\mathbf{X}_e+\mu\mathbf{X}_q)\cdot\mathbf{J}_e+(\nabla T+T\mathbf{X}_q)\cdot\mathbf{J}_s\equiv0,$$

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

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

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

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

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

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

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

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

$$L_{ee}=M_{ee}, \tag{16}$$

$$TL_{es}=M_{eq}-\mu M_{ee}. \tag{17}$$

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

Finally, if we substitute into (8) the expressions (4) for $\mathbf{J}_s$, (15) for $\mathbf{J}_q$, and (3) for $\mathbf{J}_e$, collect terms in ∇T and equate to zero, since $\nabla\bar{\mu}$ and ∇T are independent variables, we find with the help of (16) and (17),

$$T^2 L_{ss} = M_{qq} - 2\mu M_{eq} + \mu^2 M_{ee}. \tag{18}$$

Consider now an isothermal cylindrical rod as in Fig. 1, in which there is a steady electronic current $\mathbf{J}_e$ particles per second per unit area; setting $\nabla T = 0$ in (3), (4), (14), and (15) and taking the ratios of entropy and heat flows to particle current, we get

$$(\mathbf{J}_s/\mathbf{J}_e)_{\nabla T=0} = L_{es}/L_{ee} \equiv S^*, \tag{19}$$

$$(\mathbf{J}_q/\mathbf{J}_e)_{\nabla T=0} = M_{eq}/M_{ee} \equiv Q^*. \tag{20}$$

The very important quantities S^*, the "transport entropy per particle" and Q^*, the "transport heat per particle," are the parameters which we have previously mentioned as being of special importance in the thermodynamic theory of steady-state processes. We can find other relations which bring out the physical significance of the transport quantities S^* and Q^* by solving (3) for $\nabla\bar{\mu}$ and putting the result into (4), and by solving (14) for $\nabla\bar{\mu}$ and substituting into (15). In each case, after collecting terms in $\mathbf{J}_e$ and in ∇T, if we use relations (19) and (20) we find

$$\mathbf{J}_s = S^*\mathbf{J}_e + (1/L_{ee})(L_{es}^2 - L_{ee}L_{ss})\nabla T, \tag{21}$$

$$\mathbf{J}_q = Q^*\mathbf{J}_e + (1/TM_{ee})(M_{eq}^2 - M_{ee}M_{qq})\nabla T. \tag{22}$$

For a single homogeneous chemical phase under constant pressure the coefficients L_{ee}, L_{es}, L_{ss} and M_{ee}, M_{eq}, M_{qq} are functions only of the temperature, provided there is no magnetic field,[1,2] and since S^* and Q^* are defined in terms of some of these coefficients by (19) and (20), so too are S^* and Q^* functions only of the temperature for a given phase. If in Fig. 1, therefore, we imagine the current densities and temperature gradients to be uniform over a given cross section, relation (21) for example has the following significance. The axial flow of entropy consists of two terms, the first proportional to the number of particles per second crossing unit area, each particle transporting an amount S^*, and the second proportional to the temperature gradient at the cross section. If electrical current flows in an isothermal phase, we already have the relations (19) and (20). If no electrical current flows but there is a temperature gradient, (21) and (22) both lead to Fourier's law, if we write $\mathbf{J}_q = T\mathbf{J}_s$; but from (7) we see that this last equality is valid only for $\mathbf{J}_e = 0$.

Next we find the relationship between the transport quantities S^* and Q^*. This can be done by equating the factors in front of the ∇T in Eqs. (3) and (14) for $\mathbf{J}_e$, then using (19) and (20). A shorter way is to use (7), (21), and (22) in the special case of $\nabla T = 0$. Thus we can find the important relation

$$TS^* = Q^* - \mu. \tag{23}$$

Before proceeding with the specific applications to thermoelectric effects the reader may wish to read Appendix B, in which are treated several important applications of the theory to special systems. Also, because of the fundamental importance of the potentiometric method of measuring potential differences, the reader may profit by reading Appendix C before Sec. C.

C. SEEBECK EFFECT

Imagine an arrangement like that in Fig. 2 of two chemically different phases X and R, each of which is chemically and physically homogeneous[10] and isotropic. The two phases l and L are leads and are identical homogeneous phases; we use small and capital letters to allow for differences of electrical potential in these two phases. The arrangement shown is called an $X-R$ thermocouple, and is the one used in careful and precise temperature measurements. The absolute temperature is T at the variable temperature junction between phases X and R; T_0 at the so-called reference junctions between phases l and X and between R and L; and finally T_R ("room temperature") at the bottom ends of the leads l and L which are assumed to be connected to a potentiometer kept balanced so that no electrical current flows through the thermocouple. We have indicated the electronic electrochemical potential at the several pertinent points, using the notation explained in Sec. A. Since the phases l and L are chemically identical and at A and B have the same temperature, we can easily measure their difference in electrical potential at points A and B by the use of a potentiometer.

Using Eqs. (X-10)† we can write an expression of the form

$$d\bar{\mu}^{l(T)} = -S_l^* dT, \tag{24}$$

for each phase in the circuit of Fig. 2. The transport parameter S^* is of course generally a function of the temperature. If we integrate the forms (24) for each

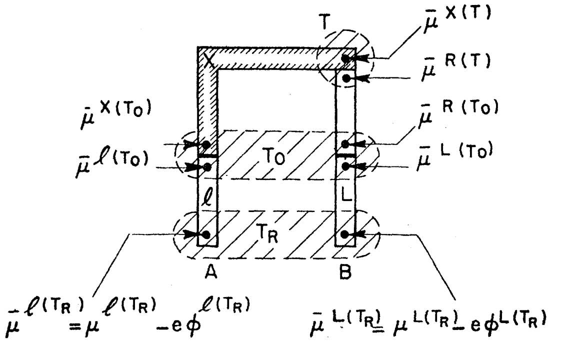

FIG. 2. Arrangement of thermocouple junctions and leads used in careful and precise temperature measurements.

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[10] Physical homogeneity includes for example uniformity of crystallite size and macroscopic uniformity of strain. The effects of inhomogeneities will be discussed in Sec. I.

† Equations X are in the appendices.

phase between the appropriate temperatures at the ends of that phase, we find the four relations

$$\left.\begin{aligned} \bar{\mu}^{l(T_0)}-\bar{\mu}^{l(T_R)}&=-\int_{T_R}^{T_0} S_l{}^*dT,\\ \bar{\mu}^{X(T)}-\bar{\mu}^{X(T_0)}&=-\int_{T_0}^{T} S_X{}^*dT,\\ \bar{\mu}^{R(T_0)}-\bar{\mu}^{R(T)}&=-\int_{T}^{T_0} S_R{}^*dT,\\ \bar{\mu}^{L(T_R)}-\bar{\mu}^{L(T_0)}&=-\int_{T_0}^{T_R} S_L{}^*dT. \end{aligned}\right\} \qquad (25)$$

Since each junction is isothermal and carries no electrical current, the electrochemical potential is continuous across each junction. Furthermore, since the electronic chemical potential in the two identical phases l and L depends only on the local temperatures, the values of $\bar{\mu}^{l(T_R)}$ and $\bar{\mu}^{L(T_R)}$ are identical. Therefore, adding the four expressions (25) and noting the order of integration, we find

$$\bar{\mu}^{L(T_R)}-\bar{\mu}^{l(T_R)}=\int_{T_0}^{T_R}(S_l{}^*-S_L{}^*)dT+\int_{T_0}^{T}(S_R{}^*-S_X{}^*)dT, \qquad (26)$$

and since $S_l{}^*=S_L{}^*$ at each temperature, (26) becomes upon separation into chemical and electrical parts,

$$\phi^{l(T_R)}-\phi^{L(T_R)}=(1/e)\int_{T_0}^{T}(S_R{}^*-S_X{}^*)dT. \qquad (27)$$

Using (23) we can express (27) in terms of the heats of transfer and the local thermostatic chemical potentials,

$$\phi^{l(T_R)}-\phi^{L(T_R)}=(1/e)\int_{T_0}^{T}[(Q_R{}^*-Q_X{}^*)-(\mu^R-\mu^X)](dT/T). \qquad (28)$$

The difference in electrical potential

$$\mathcal{E}_{XR}=\mathcal{E}_{XR}(T_0,T)\equiv\phi^{l(T_R)}-\phi^{L(T_R)}, \qquad (29)$$

is called the thermoelectric potential difference of the X-R thermocouple at temperature T and with reference junction temperature T_0. We see that, provided terminals A and B are at the same temperature, the potential difference $\mathcal{E}_{XR}$ is independent of T_R. In the symbol $\mathcal{E}_{XR}$ the second subscript indicates the reference material. The thermoelectric potential difference is usually expressed in volts, millivolts, or microvolts. Other names are usually used for $\mathcal{E}_{XR}$, such as for example "thermoelectric electromotive force," "thermal emf," and so on. We wish to avoid the unfortunate connotation "force" in this connection and we shall therefore always use the more appropriate term "potential difference."

From (27) it is seen that for a given pair of homogeneous and isotropic phases X and R the thermoelectric potential difference depends only on the temperatures T_0 and T of the junctions and not in any way upon the temperature gradients along any of the phases in the system. This fact was originally discovered empirically by Magnus[11] and is now known as the Law of Magnus.

The derivative $S_{XR}\equiv d\mathcal{E}_{XR}/dT$, of great importance in thermoelectricity, is called the relative thermoelectric power of phase X against R, or relative to R. The connotation of "power" here is also unfortunate; however, we can think of no reasonable substitute and shall therefore make use of this commonly accepted name. We shall often use the single word thermopower in place of thermoelectric power. Some writers use the terms "thermal emf" and "thermoelectric power" interchangeably, with corresponding confusion in their units; this practice is obviously deplorable. The sign convention almost universally adopted for S_{XR} is the following. In Fig. 2 suppose that $T=T_0+\Delta T$ with ΔT very small, and that therefore $\Delta\mathcal{E}_{XR}=S_{XR}\Delta T$. If for ΔT positive $\Delta\mathcal{E}_{XR}=\phi^{l(T_R)}-\phi^{L(T_R)}$ is also positive, then the relative thermoelectric power S_{XR} at temperature $T_0+(1/2)\Delta T$ is positive. Or, alternatively, if the terminals A and B of the thermocouple in Fig. 2 are connected together when $T=T_0+\Delta T$, ΔT small, the thermoelectric power S_{XR} is positive when the thermoelectrically generated current flows from the reference phase R to phase X at the warmer junction.

From (29) and (27) we find by differentiation with respect to temperature,

$$S_{XR}\equiv d\mathcal{E}_{XR}/dT=d(\phi^{l(T_R)}-\phi^{L(T_R)})/dT=(1/e)(S_R{}^*-S_X{}^*), \qquad (30)$$

which shows that the relative thermopower S_{XR} depends on the temperature T but not on the reference temperature T_R.

From (30) we can write, denoting a third homogeneous, isotropic phase by the letter A,

$$eS_{XR}=S_R{}^*-S_X{}^*=(S_R{}^*-S_A{}^*)+(S_A{}^*-S_X{}^*)=eS_{AR}+eS_{XA};$$

or

$$S_{XR}=S_{XA}+S_{AR}. \qquad (31)$$

Introducing additional homogeneous phases B, C, $\cdots$ we can extend (31) to give

$$S_{XR}=S_{XA}+S_{AB}+S_{BC}+\cdots+S_{iR}. \qquad (32)$$

Equation (32) is not particularly useful, but its special

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[11] G. Magnus, Pogg. Ann. **83**, 469 (1851).

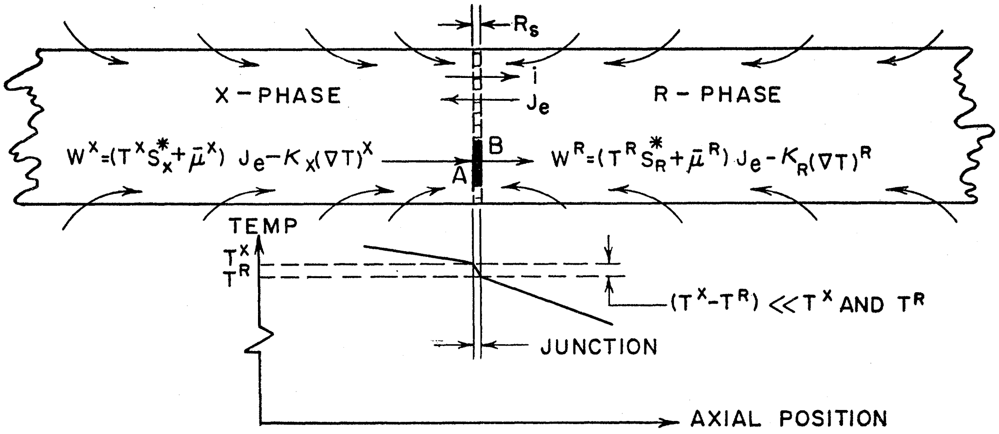

FIG. 3. The flow of energy and electrical current across a nonisothermal junction between two chemically different phases. The Peltier coefficient is $\Pi_{XR}\equiv-(T/e)(S_R{}^*-S_X{}^*)$.

case (31) is of great importance in that it allows one to determine the relative thermopowers of two phases X and R if the relative thermopower of each is known against a third phase A. Or, conversely, if each of the three relative thermopowers in (31) has been determined separately by experiment, the extent to which these values satisfy (31) is a measure of the reliability of the data and of the homogeneity of the phases used.

D. PELTIER EFFECT AT A JUNCTION BETWEEN DISSIMILAR PHASES

The total energy flow density $\mathbf{W}$ in a phase X is given by Eq. (5),

$$\mathbf{W}^X=\mathbf{Q}^X+\bar\mu^X\mathbf{J}_e=T\mathbf{J}_s{}^X+\bar\mu^X\mathbf{J}_e. \tag{33}$$

Using (21) and (X-8) we find that Eq. (33) becomes

$$\mathbf{W}^X=T^*S_X{}^*\mathbf{J}_e+\bar\mu^X\mathbf{J}_e-\kappa_X(\nabla T)^X; \tag{34}$$

a similar expression can be written for the R phase when the particle current density $\mathbf{J}_e$ is the same in both phases:

$$\mathbf{W}^R=T^RS_R{}^*\mathbf{J}_e+\bar\mu^R\mathbf{J}_e-\kappa_R(\nabla T)^R. \tag{35}$$

The quantities in Eqs. (34) and (35) refer, respectively, to the values just to the left and just to the right of the element AB of the junction in Fig. 3. The curved arrows across the boundaries of the phases X and R indicate an exchange of heat between a reservoir and the phases. Thus the axial components of the vectors $\mathbf{W}$ and ∇T as well as the values of $\bar\mu$ and κ would in general vary as we moved away from the junction, and we should focus our attention on the values in the immediate vicinity of the element AB. We want to consider here only the steady-state situation so that if we apply the energy conservation law to the energy passage through element AB, assuming a very thin junction we must have $\mathbf{W}^R=\mathbf{W}^X$ or

$$\begin{aligned}T^RS_R{}^*\mathbf{J}_e-\kappa_R(\nabla T)^R+\bar\mu^R\mathbf{J}_e\\=T^XS_X{}^*\mathbf{J}_e-\kappa_X(\nabla T)^X+\bar\mu^X\mathbf{J}_e.\end{aligned} \tag{36}$$

Now in any ordinary junction between two phases X and R the axial extent of the junction will be very small compared with the lateral dimensions of the cylinders of these phases, as in Fig. 3, so that as indicated in the schematic variation of temperature T in the lower part of this figure the temperature difference T^X-T^R will be very small compared with both T^R and T^X. Therefore we make the assumption hereafter that $T^X=T^R\equiv T$. Equation (36) can then be written

$$\begin{aligned}T(S_R{}^*-S_X{}^*)\mathbf{J}_e+(\bar\mu^R-\bar\mu^X)\mathbf{J}_e\\-[\kappa_R(\nabla T)^R-\kappa_X(\nabla T)^X]=0.\end{aligned} \tag{37}$$

The difference between the (isothermal) electrochemical potentials $\bar\mu^R$ and $\bar\mu^X$ is given by (X-17); namely, with the electric current i flowing rightward from phase X to phase R,

$$\bar\mu^R-\bar\mu^X=eiR_s=e|\mathbf{J}|AR_s=-e^2|\mathbf{J}_e|AR_s. \tag{38}$$

The second quantity in (37) is then

$$(\bar\mu^R-\bar\mu^X)|\mathbf{J}_e|=(eiR_s)\cdot(-i/Ae)=-(1/A)(i^2R_s), \tag{39}$$

which represents the Joule heat developed each second per unit cross section of the junction. According to Eq. (X-17) the *electronic* electrochemical potential *increases* along the current (i) direction; the electrochemical potential of a *positive* charge would *decrease* along the current direction. Equation (39) refers of course to the electronic electrochemical potential. The first term in (37) written with total current i is

$$T(S_R{}^*-S_X{}^*)|\mathbf{J}_e|=-(T/e)(S_R{}^*-S_X{}^*)(i/A).$$

Substitution of this expression and (39) into (37) then gives

$$\begin{aligned}-(T/e)(i/A)(S_R{}^*-S_X{}^*)-(i^2/A)R_s\\-|\kappa_R(\nabla T)^R-\kappa_X(\nabla T)^X|=0.\end{aligned} \tag{40}$$

We now set

$$\Pi_{XR} \equiv -(T/e)(S_R^* - S_X^*), \tag{41}$$

and upon substitution into (40) we find the very useful relation

$$(i/A)\Pi_{XR} - (i^2/A)R_s - |\kappa_R(\nabla T)^R - \kappa_X(\nabla T)^X| = 0. \tag{42}$$

We call the quantity Π_{XR} the Peltier coefficient between the X and R phases.

Referring to Eq. (42) and to the temperature diagram in Fig. 3, we see that it will always be possible to force the temperature distribution to be flat at least in the immediate vicinity of the junction, so that the bracketted term in (42) vanishes. In this case the junction is said to be isothermal, and we have

$$i\Pi_{XR} - i^2R_s = 0, \quad \text{for} \quad (\nabla T)^R = (\nabla T)^X = 0. \tag{43}$$

This means that in an isothermal junction in the steady state, the Peltier heat $i\Pi_{XR}$ is exactly balanced by the Joule heat produced at the junction, provided the total current i is such as to satisfy (43) both in magnitude and in sense. The sense for positive i is indicated in Fig. 3; namely, positive i means that the current (not electrons) goes across the junction from phase X to phase R. If i is in the opposite direction, i negative, it is impossible to satisfy (43) and we no longer have a steady state: the temperature distribution of the junction region will change with time. The argument given implies that the coefficient Π_{XR} is positive, and that for positive i and positive Π_{XR} the Peltier effect operates so as to make the junction behave like a heat sink, absorbing the always positive Joule heat produced. Thus our arbitrary convention that positive i means current flow from X to R fixes the sign convention for the Peltier coefficient; that is, a positive Peltier coefficient Π_{XR} means that when current flows across the junction from X to R, heat must be supplied to the junction in order to maintain a steady state.

Equation (43) tells us that a steady-state, isothermal junction can be maintained by a balance between the Peltier heat (sink) and the Joule heat (source) only for a special value and sense of the current, say i_0. For a current in the same sense but less than i_0, we need to inject by some means or other an additional amount of heat $(i_0 - i)\Pi_{XR}$ or $R_s(i_0^2 - i^2)$ in order to maintain the original isothermal steady-state situation. If the current i is in the opposite direction, heat must be removed; and if R_s is not zero we must remove not only the generated Peltier heat (now a heat source) but also the always positive Joule heat. In short, in order to maintain an isothermal steady-state junction, we must somehow inject into the junction a Peltier heat $i\Pi_{XR}$ which may be positive (add heat) or negative (remove heat) depending upon the signs of both Π_{XR} and i.

It has been customary in discussions of the Peltier effect to treat only an isothermal junction without resistance, thus leaving out of the analysis the Joule heating and the flow of heat across sections near the junction. The usual procedure is to state simply, instead of our Eq. (42), that in the steady state

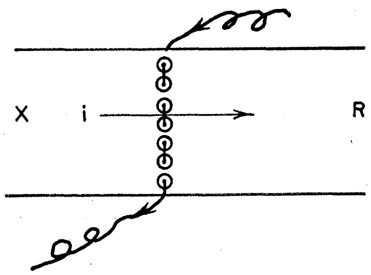

FIG. 4. Hypothetical arrangement for measuring Peltier heat at a junction. The arrangement is a poor one for actual laboratory use, but illustrates the meaning of the Peltier heat under certain conditions, as explained in the text.

$$\{\text{heat injected or removed at the junction}\} = i\Pi_{XR}, \tag{44}$$

without giving the details of how the heat is added or removed at the junction. What we wish to point out is that, while this procedure leads to a perfectly legitimate definition of the Peltier coefficient, it invokes a somewhat hypothetical experimental arrangement which has in fact rarely if ever been used for the measurement of Peltier heat. In Fig. 4 the small circles represent holes drilled through the rods X and R at their junction, and the dots inside the circles represent very fine resistance wire threaded through the holes and electrically insulated so as to form an "internal junction-heater element" located right in the plane of the junction itself. The diminution of the cross section will of course increase the effective junction resistance and the electrical current paths will become very complicated in the vicinity of the junction. However, we can suppose that for all practical purposes the heater is a strictly planar heater located exactly in the plane of the junction and that the total junction resistance is negligible. Even if this supposition were to be well fulfilled there is still the difficulty that the arrangement can be used only when the Peltier heat $i\Pi_{XR}$ is positive.

The usual way to measure $i\Pi_{XR}$ is to enclose the junction in a small calorimeter and to measure the total heat absorbed from or given out in a certain time interval to a fluid in which the junction is immersed. Corrections are made for the Joule term in Eq. (42), and one method for doing this is to use alternating current to determine the Joule heat separately. The calorimetric method involves essentially a measurement of the surface integral of heat-flow terms of form $\kappa\nabla T$ at the surface of each phase, the integral taken over the whole surface of contact between phases and surrounding fluid. Strictly speaking, most Peltier heat measurements made calorimetrically do not involve a steady-state condition of the junction, and the resulting value for the Peltier coefficient represents a complicated mean value for the temperature range

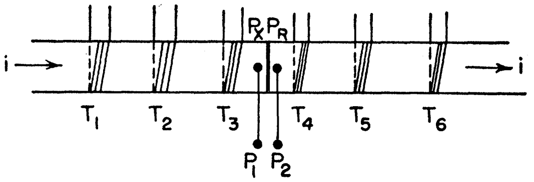

FIG. 5. Scheme for the direct measurement of Peltier heat at a nonisothermal junction, making direct use of Eq. (42). The temperature gradient is measured by means of resistance thermometers T_1, T_2, $\cdots T_6$.

between the initial and final temperatures. However, since the Peltier coefficient for most metals varies slowly with temperature, any errors resulting from this effect are most likely much smaller than the remaining errors. In short, we may say that the usual experimental methods for determining Π_{XR} make indirect use of Eq. (42).

A determination of Π_{XR} by direct use of (42) seems to be feasible and could be carried out with an arrangement like the one sketched in Fig. 5. The specimens X and R are in the form of rods jointed as shown, and have mounted on them three resistance thermometers each. Only two thermometers on each rod are needed to determine the temperature gradients in (42) if the heat flow is strictly axial, and the third thermometer is used to determine whether the flow is actually completely axial. If the flow is not axial the reading of the third thermometer can be used to make whatever slight corrections are necessary. The entire composite rod is enclosed in a radiation shield whose temperature distribution can be kept close to that in the rods, thereby making the distribution in the rods very accurately linear. The rod and shield are in an evacuated container. A knowledge of the bracketted term in (42) still requires the values of the thermal conductivities κ_X and κ_R as well as their temperature variation if we desire the value of Π_{XR} over a range of temperatures. However, by forcing $(\nabla T)^X$ to vanish by means of auxiliary heaters at the ends of the rods we can always eliminate the term $\kappa_X(\nabla T)^X$, so that if phase R is the "reference phase" we measure (or look up in tables) its κ_R *vs* temperature once and for all, and need not know κ_X at all.

The Joule term in (42) is easily known once the contact resistance is known in its dependence on temperature. We give in Appendix D a brief analysis of the usual laboratory method for determining the contact resistance between dissimilar metal wires.

Having found R_s from Eq. (X-63) and having previously shown how the heat conduction term in (42) may be evaluated, we are in a position to deduce the value of the Peltier heat term $i\Pi_{XR}$ in (42). Obviously the Peltier heat experiment is carried out with a nonisothermal junction, possibly with $(\nabla T)^X=0$, while the necessary determination of R_s is made as pointed out in Appendix D with the junction region (Fig. 28) maintained isothermal. The determinations of Π_{XR} and R_s of course refer to the values at the same temperature T in Fig. 28 and $T\equiv T^X\cong T^R$ in Fig. 3. So far as the writer knows, this method for the direct determination of the Peltier heat has never been used. A rough estimate of the precision required in the measurement of the gradient $(\nabla T)^R$ makes the method seem feasible.

It will be shown in Sec. F that the Peltier coefficient is related to the relative thermopower of an X-R thermocouple by $-\Pi_{XR}=TS_{XR}$, where T is the absolute temperature of the junction. Equation (31) gives the additivity rule for thermopowers, and so we have also an additivity rule for Peltier coefficients, namely

$$\Pi_{XR}=\Pi_{XA}+\Pi_{AR}. \tag{45}$$

Finally, we should like to comment on the phrase "Peltier emf" which is sometimes found in the literature. If we write the first two terms in (42) in the form $(\Pi_{XR}-iR_s)i$, having first multiplied through by the area A, we see that each term in parentheses has the dimensions of an electrical potential and can therefore be expressed in volts. If we separate (X-17) into chemical and electrical portions we find

$$\phi^R-\phi^X=-iR_s+(\mu^R-\mu^X), \tag{46}$$

showing that in general the product iR_s cannot be called the jump in *electrical* potential across the junction unless the phases X and R happen to have identical *chemical* potentials. In particular, if the phases X and R are chemically identical, the quantity iR_s will in fact be just the jump in electrical potential across the junction. Thus the electrochemical, the chemical, and the electrical potential changes across the junction being related as in (X-17) and (46) above, there is nothing left to call a "Peltier potential difference" or "Peltier emf."

E. THOMSON EFFECT

Consider a uniform cylindrical rod of a single homogeneous and isotropic phase as in Fig. 6, in which there is an arbitrary temperature distribution and through the surface of which heat is transferred to or from the surroundings. There is at first no electrical current through the phase. V is the volume between cross sections A and B. The temperature at points in cross section A is $T=T(r)$ and at points in section B is $T'=T'(r)$, r denoting position within the section. The temperature gradients at points in sections A and B are $\mathbf{G}(r)$ and $\mathbf{H}(r)$, respectively, both temperature and gradients varying throughout each cross section. We formulate the following problem: If we pass a total electrical current i through the cylinder, how much total heat must pass per second across the cylindrical surface between sections A and B in order to maintain the original temperature distribution and consequently also the original temperature-gradient distribution?

The total energy current across section A without electrical current is found from Eq. (34) to be

$$\int_A \mathbf{W}^A\cdot d\mathbf{a} = -\int_A \kappa(T)\mathbf{G}(r)\cdot d\mathbf{a}, \tag{47}$$

where $d\mathbf{a}$ is an area element in cross section A and the integral is of course taken over the entire cross section. Similarly, over section B the total energy current is given by

$$\int_B \mathbf{W}^B\cdot d\mathbf{a} = -\int_B \kappa(T')\mathbf{H}(r)\cdot d\mathbf{a}, \tag{48}$$

the prime referring to the local values in the section B. Now with total current i flowing the total energy flow rate across A is

$$\int_A [-(1/e)(TS^*+\bar{\mu})\mathbf{J}-\kappa(T)\mathbf{G}(r)]\cdot d\mathbf{a}, \tag{49}$$

since the $T(r)$ and $\mathbf{G}(r)$ distributions are the same as in (47); and similarly across B the total energy flow rate is

$$\int_B [-(1/e)(T'S^{*\prime}+\bar{\mu}')\mathbf{J}'-\kappa(T')\mathbf{H}(r)]\cdot d\mathbf{a}, \tag{50}$$

the primes again referring to the local values of the respective parameters in the cross section B. The excess total energy flow rate *out* across section B over the flow rate in across A before i is turned on is (48) minus (47) or

$$E_0 \equiv -\int_B \kappa(T')\mathbf{H}(r)\cdot d\mathbf{a} + \int_A \kappa(T)\mathbf{G}(r)\cdot d\mathbf{a}, \tag{51}$$

while the corresponding excess with current i is (50) minus (49) or

$$\begin{aligned} E_i \equiv -(1/e)\int_B (T'S^{*\prime}+\bar{\mu}')\mathbf{J}'\cdot d\mathbf{a} \\ +(1/e)\int_A (TS^*+\bar{\mu})\mathbf{J}\cdot d\mathbf{a} - \int_B \kappa(T')\mathbf{H}(r)\cdot d\mathbf{a} \\ +\int_A \kappa(T)\mathbf{G}(r)\cdot d\mathbf{a}. \end{aligned} \tag{52}$$

The necessary additional rate of influx of energy in the form of heat across the cylindrical boundary between sections A and B in order to maintain the same temperature (and temperature-gradient) distribution as without electrical current is thus given by (52) minus (51), or

$$\begin{aligned} \Delta E \equiv E_i - E_0 = -(1/e)\int_B (T'S^{*\prime}+\bar{\mu}')\mathbf{J}'\cdot d\mathbf{a} \\ +(1/e)\int_A (TS^*+\bar{\mu})\mathbf{J}\cdot d\mathbf{a}. \end{aligned} \tag{53}$$

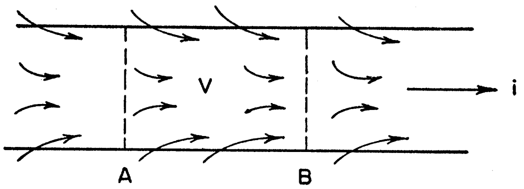

FIG. 6. The cylinder of uniform chemical composition has a certain original, steady-state temperature distribution before an electrical current passes through it. If a current i now is made to flow along the cylinder, how much total heat ΔE must pass in the steady state per second across the cylindrical surface between cross sections A and B in order to maintain the original temperature distribution? The solution to the problem is given by Eq. (59).

Each of the quantities in the integrand in (53) has a value depending upon position within each cross section; for example, T at a certain point in cross section A is not necessarily the same as T' at the geometrically corresponding point in section B. In particular, although the surface integrals of the electrical current densities $\mathbf{J}$ and $\mathbf{J}'$ over their respective sections A and B must of course be the total current i, the densities $\mathbf{J}$ and $\mathbf{J}'$ themselves are not necessarily the same at corresponding points in the two sections.

The integral (53) represents the surface integral of the vector quantity $(TS^*+\bar{\mu})\mathbf{J}$ over the cross sections A and B. But since there is no electrical current across the cylindrical boundary of the phase, the integral can also be written as extending over the entire closed cylindrical surface including the ends A and B. This extension then allows us to use Gauss' theorem to write

$$\begin{aligned} e\Delta E = -\int_{\substack{\text{entire closed}\\ \text{surface}}} (TS^*+\bar{\mu})\mathbf{J}\cdot d\mathbf{a} \\ = -\int_V \nabla\cdot[(TS^*+\bar{\mu})\mathbf{J}]dv, \end{aligned} \tag{54}$$

dv being a volume element and the volume integral extending over the whole volume of the cylinder between Secs. A and B. The integrand in the volume integral becomes, since $\nabla\cdot\mathbf{J}=0$,

$$\begin{aligned} \mathbf{J}\cdot\nabla(TS^*+\bar{\mu})+(TS^*+\bar{\mu})\nabla\cdot\mathbf{J} \\ = \mathbf{J}\cdot[T\nabla S^*+S^*\nabla T+\nabla\bar{\mu}]; \end{aligned}$$

solving (3) for $\nabla\bar{\mu}$, using (19), (X-7) and $\mathbf{J}=-e\mathbf{J}_e$ we find

$$\mathbf{J}\cdot[T\nabla S^*+S^*\nabla T+\nabla\bar{\mu}] = T\mathbf{J}\cdot\nabla S^* + (e/\sigma)\mathbf{J}^2. \tag{55}$$

Putting this into (54) we get

$$e\Delta E = -\int_V T\mathbf{J}\cdot\nabla S^* dv - e\int_V (1/\sigma)\mathbf{J}^2 dv. \tag{56}$$

The second integral represents the total Joule heat generated per second by the current and is seen to be always positive. In the first integral, since S^* depends only on temperature we can write $\partial S^*/\partial x = (\partial S^*/\partial T) \times (\partial T/\partial x)$ and similar expressions for the y and z components of ∇S^*, so that $\nabla S^* = (\partial S^*/\partial T)\nabla T$. The expression (56) thus becomes

$$e\Delta E = -\int_V (T\partial S^*/\partial T)\mathbf{J}\cdot\nabla T dv - e\int_V (1/\sigma)\mathbf{J}^2 dv, \quad (57)$$

or if we set[12]

$$\tau \equiv -(1/e)T(\partial S^*/\partial T), \quad (58)$$

we get finally

$$\Delta E = \int_V \tau\mathbf{J}\cdot\nabla T dv - \int_V (1/\sigma)\mathbf{J}^2 dv. \quad (59)$$

Equation (59) gives us the solution to the problem formulated at the beginning of this section; namely, if when there is no electrical current flowing through the cylinder there is a given initial, steady-state temperature distribution, then if the cylinder is to have this same distribution after the electrical current is turned on and a steady state is again established, we must add total heat to the volume V of the cylinder at the total rate given by Eqs. (59) and (58). The rate at which heat must be added *per unit volume* depends upon the location of the small volume element within the phase and is given by

$$\Delta E/\Delta v = \tau\mathbf{J}\cdot\nabla T - (1/\sigma)\mathbf{J}^2. \quad (60)$$

The parameter $\tau = \tau(T)$ is called the Thomson coefficient and the first term in either (60) or (59) is called the Thomson heat, although of course these terms actually represent rates of adding heat. If $\Delta E/\Delta v$ is expressed in watts per unit volume the Thomson coefficient has the dimensions of an electrical potential per degree and can be expressed in volts per degree.

Equation (59) gives the relation between the Thomson heat and the total rate of heat addition to the volume V of the phase, and in order to determine τ itself we must apply (59) to an experimental arrangement in which we can remove τ from under the integral sign. This can be done most easily by applying (59) to a long section of thin wire such as indicated in Fig. 7, in which the temperature gradient and electrical current density are assumed very nearly uniform throughout each cross section of area ΔA. The distance between regions of temperature T and $T+\Delta T$ is taken to be Δx. In this case the Thomson heat term in (59) reduces to the following simple form, where now $J \equiv |\mathbf{J}|$,

$$\int_V \tau\mathbf{J}\cdot\nabla T dv = \tau(\Delta T/\Delta x)\Delta x\cdot(J\cdot\Delta A) = \tau i\Delta T, \quad (61)$$

and the Joule heat term reduces to

$$-\int_V (1/\sigma)J^2 dv$$
$$= -(1/\sigma)(\Delta x/\Delta A)(\Delta A\cdot J)(\Delta A\cdot J) = -i^2 R, \quad (62)$$

giving therefore the experimentally usable relation

$$\Delta E = \tau i\Delta T - i^2 R, \quad (63)$$

where R is the total resistance of the length Δx of wire. The length Δx of wire, total resistance R, is held in a steady state with a small temperature gradient $\Delta T/\Delta x$ and total electrical current i flowing through it. By measuring ΔE (watts) calorimetrically, knowing i, ΔT, and R we can use (63) to find the Thomson coefficient $\tau = \tau(T + \frac{1}{2}\Delta T)$.

FIG. 7. A long, thin wire may be used in the determination of the Thomson coefficient by making use of Eq. (63), which is a special case of Eq. (59).

Since the various factors in (58) depend only on the absolute temperature T, we can integrate (58) to find the transport parameter S^* in terms of the Thomson coefficient, and the resulting expression is defined as the absolute thermoelectric power or absolute thermopower of the homogeneous isotropic chemical phase at temperature T; namely,

$$S^{\text{abs}} \equiv -(1/e)S^* = \int_0^T (\tau/T)dT. \quad (64)$$

From (30) and (64) it follows that the relative thermopower S_{XR} of a thermocouple made of two phases X and R can be found from the difference between their absolute thermopowers; that is

$$S_{XR} = S_X{}^{\text{abs}} - S_R{}^{\text{abs}}$$
$$= \int_0^T (\tau_X/T)dT - \int_0^T (\tau_R/T)dT. \quad (65)$$

De Groot[2] has derived the thermoelectric potential difference by using two "homogeneous effect" terms of the form (X-12) for the two phases X and R added to two "heterogeneous" or "contact potential" terms of the form (X-46). One often finds the first terms referred to as "Thomson emf's" and the second terms referred to as "Peltier emf's." We have already discussed in Sec. D the inappropriateness of the latter term. The name "Thomson emf" is in our opinion equally undesirable, inasmuch as the "homogeneous" term (X-12) is related to the Thomson coefficient only through the integral relation (64) above, leaving still the term $(1/e)(\partial\mu/\partial T)$ in (X-12). In fact, if we add together the four terms mentioned, namely two of form (X-12) and two of form (X-46), we find for the thermo-

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[12] Callen and de Groot (references 1 and 2) have a plus sign in (58), but their charge carrier is positive whereas ours is $-e$ for the electron.

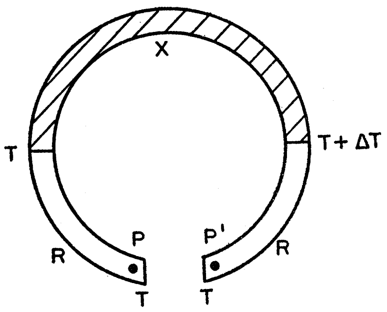

FIG. 8. The thermoelectric potential difference between points P and P' may be expressed as the difference between two "homogeneous thermoelectric potential" differences plus the difference between two "heterogeneous" or "contact potential" differences, according to Eqs. (66) and (67).

electric potential difference of the thermocouple in Fig. 8 the expression

$$\Delta\mathcal{E}_{XR}=\frac{1}{e}\left(\frac{\partial\mu^R}{\partial T}+S_R{}^*\right)\Delta T+\left[\phi^{X(T+\Delta T)}-\phi^{R(T+\Delta T)}\right]$$

$$-\frac{1}{e}\left(\frac{\partial\mu^X}{\partial T}+S_X{}^*\right)\Delta T-\left[\phi^{X(T)}-\phi^{R(T)}\right]. \quad (66)$$

From (X-46) we get

$$\left[\phi^{X(T+\Delta T)}-\phi^{R(T+\Delta T)}\right]-\left[\phi^{X(T)}-\phi^{R(T)}\right]$$

$$=\frac{\partial}{\partial T}(\phi^X-\phi^R)\Delta T=-\frac{1}{e}\frac{\partial}{\partial T}(\mu^X-\mu^R)\Delta T, \quad (67)$$

and substituting (67) into (66) gives simply

$$\Delta\mathcal{E}_{XR}=(1/e)(S_R{}^*-S_X{}^*)\Delta T, \quad (68)$$

the same result as in (30). Thus the "contact potential" or "heterogeneous" terms (67) are canceled by a portion (the thermostatic portion!) of the "homogeneous" terms (X-12).

Finally, we can picture the origin of the thermoelectric potential difference in a thermocouple in the following way. From (64) and (X-10) we can see that a temperature gradient in a homogeneous isotropic phase X gives rise to an electronic electrochemical gradient which is characteristic of phase X alone, apart from whether or not this phase is connected electrically to any other phase as in a thermocouple. This electrochemical gradient can be determined from (X-10) once the integral (64) has been evaluated from an experimental measurement of the Thomson coefficient and its variation with temperature. Thus in Fig. 9 if the temperature is initially uniform at T throughout the entire system the electrochemical potential will be uniform throughout. The temperature of the entire upper portion is now raised a small amount ΔT. The electrochemical potential will in general change everywhere in the system, but will have a uniform value in the lower isothermal region at temperature T. We use this value as the zero level or reference level, and the electrochemical potentials at the upper ends of X and R become with respect to this level $\Delta\bar{\mu}^X=-S_X{}^*\Delta T$ and $\Delta\bar{\mu}^R=-S_R{}^*\Delta T$, respectively. The difference between these electrochemical potentials can be measured potentiometrically by connecting two sections R and r of chemically identical and isothermal phases as shown by the upper dotted regions in Fig. 9. Thus the measured thermoelectric potential difference is

$$\Delta\mathcal{E}_{XR}=\phi^R-\phi^r=(1/e)\Delta\bar{\mu}^X-(1/e)\Delta\bar{\mu}^R$$

$$=(1/e)(S_R{}^*-S_X{}^*)\Delta T, \quad (69)$$

the same as in (30) and (68).

F. THE KELVIN RELATIONS OF THERMOELECTRICITY

From Eqs. (30), (41), and (58) giving thermopower, Peltier coefficient, and Thomson coefficient in terms of the transport entropy per particle S^*, we can now easily derive the following relationships between the three thermoelectric parameters, known as the Kelvin thermoelectric relations:

$$\Pi_{XR}=-TS_{XR}, \quad (70)$$

$$\tau_X-\tau_R=T(\partial S_{XR}/\partial T). \quad (71)$$

Having settled on a sign convention for each of the quantities Π_{XR} and S_{XR}, we can thereby fix the sign in (70), as can be seen from the following argument. Imagine a closed thermocouple circuit made of two phases X and R as in Fig. 10. If the relative thermopower S_{XR} of the couple is positive, current will flow in the direction of the arrows when the right-hand junction is ΔT degrees warmer than the left-hand junction. When the current flows in this direction the left-hand junction must become a heat source and the right junction a sink. For if the reverse were true, the left junction would cool further and the right junction would become still hotter, thereby increasing the

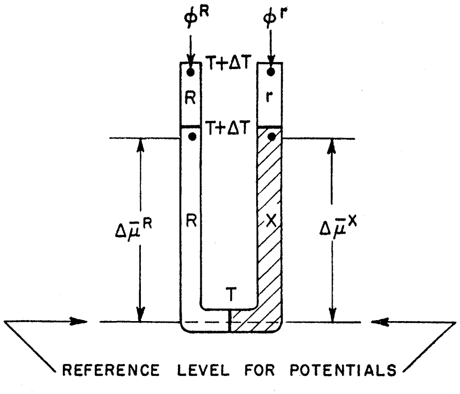

FIG. 9. The thermoelectric potential difference $\phi^R-\phi^r$ is simply $(1/e)$ times the difference $\Delta\bar{\mu}^X-\Delta\bar{\mu}^R$, the electrochemical potential changes being brought about by the temperature change ΔT; thus $\Delta\bar{\mu}^X=-S_X{}^*\Delta T$ and $\Delta\bar{\mu}^R=-S_R{}^*\Delta T$.

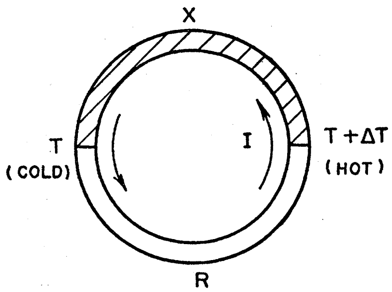

FIG. 10. This thermocouple circuit is used to explain the minus sign in the Kelvin relation (70).

thermoelectric current. This current increase would result in still further cooling of the left junction and further heating of the right, and so on. Once started with a minute ΔT this thermocouple device would thus generate an increasing current and would furthermore cool the left junction without any external interaction. This being impossible we conclude that if the relative thermopower S_{XR} is positive, the left-hand junction in Fig. 10 must become a heat source so that with the current I crossing the X-R junction in the direction from X to R the Peltier heat must be negative. This explains the minus sign in Eq. (70).

The relations between the various thermomagnetic coefficients (Hall, Nernst, Ettingshausen, Righi-Leduc) have been found by Callen.[13]

G. ANISOTROPY OF THERMOELECTRIC EFFECTS

According to Eq. (21) a particle current density J_e flowing in an isothermal rod has associated with it an entropy current density given by $J_s=S^*J_e$, in which the transport entropy per particle S^* depends on the chemical nature of the phase and on the temperature. The value of this parameter S^* for a given kind of particle (electron, say) in a given phase is determined by the detailed way in which the particle is scattered as it passes through the atomic lattice of the phase. One would not be too surprised, therefore, to find that in a single crystal the value of S^* for a given charge carrier depends in general upon the crystallographic direction in which the carrier moves or drifts. Since the absolute thermoelectric power of a phase is determined by S^* it would follow that the thermoelectric properties of a (noncubic) single crystal would vary with crystallographic direction. This is in fact the case, and a considerable amount of thermoelectric data is available on such pure metal single crystals as zinc, cadmium, antimony, bismuth, tin, and magnesium.[14] We wish to discuss next the theoretical aspects of thermoelectric anisotropy. We begin by postulating a tensor formulation of the fundamental thermoelectric equations applicable to any crystalline or otherwise nonisotropic as well as nonhomogeneous medium. We then apply the general equations to special crystal systems; of particular importance is the application to "uniaxial" crystals, since these are the ones most extensively studied experimentally. The applications of the general theory lead to the Kelvin symmetry relations and to Bridgman's "internal Peltier effect." Finally, we compare our formulation with those of Kelvin, Bridgman, Ehrenfest and Rutgers, Meissner, Kohler, and Meixner.

1. The General Equations for Anisotropic Media

We use as a starting point the combination of relations (21) and (X-8), namely[15]

$$\mathbf{J}^s=S^*\mathbf{J}^e-(\kappa/T)\nabla T. \tag{72}$$

In setting up the general equations *we make the assumption that each component of the entropy current density J_i^s is a linear function of the components J_j^e, of particle current density and of the components $\nabla_j T$ of the temperature gradient*, with i, $j=1,2,3$. The temperature T and the electrochemical potential $\bar{\mu}$ are considered as continuous and differentiable functions of position (x_1, x_2, x_3) within each phase. If an electrical current flows across a boundary between two media, there will be cases (as mentioned in Example 6 of Appendix B) in which the electrochemical potential cannot be defined *within* the junction. In such cases, however, the finite jump in $\bar{\mu}$ across the junction can be defined and one needs only to use the appropriate boundary conditions for $\bar{\mu}$; otherwise such cases introduce no particular difficulties. The relation (72) is thus replaced by the three equations[16]

$$J_i^s=S_{ij}^*J_j^e-(\kappa_{ij}/T)(\partial T/\partial x_j), \quad i, j=1, 2, 3, \tag{73}$$

in which the quantities S_{ij}^* form the *transport entropy matrix* and the κ_{ij} form the *heat conductivity matrix.* We emphasize the fact that the equations (73) are postulates, reasonable extensions of the isotropic Eq. (72), and that their validity must be checked by experiment. At the present time there is available only information on crystals of comparatively high symmetry, to which the simpler Kelvin and Kohler symmetry relations are supposedly applicable. Although the Kelvin-Kohler relations appear to be quite well satisfied by available data on such crystals, there is still need for further and more extensive measurements on single crystals over large temperature ranges.

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[13] H. B. Callen, Phys. Rev. **85**, 16 (1952).

[14] W. Meissner, *Handbuch der Experimentalphysik* (Leipzig, 1935), vol. XI, pt. 2.

[15] We shall hereafter write the subscripts s and e in (72) as superscripts to make room for the subscript indices i and j.

[16] The presence of two identical subscripts indicates a summation. Thus (73) is shorthand notation for the three components

$$J_1^s=S_{11}^*J_1+S_{12}^*J_2+S_{13}^*J_3-\frac{1}{T}\left(\kappa_{11}\frac{\partial T}{\partial x_1}+\kappa_{12}\frac{\partial T}{\partial x_2}+\kappa_{13}\frac{\partial T}{\partial x_3}\right),$$

$$J_2^s=S_{21}^*J_1+S_{22}^*J_2+S_{23}^*J_3-\frac{1}{T}\left(\kappa_{21}\frac{\partial T}{\partial x_1}+\kappa_{22}\frac{\partial T}{\partial x_2}+\kappa_{23}\frac{\partial T}{\partial x_3}\right),$$

$$J_3^s=S_{31}^*J_1+S_{32}^*J_2+S_{33}^*J_3-\frac{1}{T}\left(\kappa_{31}\frac{\partial T}{\partial x_1}+\kappa_{32}\frac{\partial T}{\partial x_2}+\kappa_{33}\frac{\partial T}{\partial x_3}\right).$$

It follows from (73) and (6) that the total energy current density W_i can be written

$$W_i = TS_{ij}^* J_j^e + \bar{\mu} J_i^e - \kappa_{ij}(\partial T/\partial x_j)$$
$$= (TS_{ij}^* + \bar{\mu}\delta_{ij}) J_j^e - \kappa_{ij}(\partial T/\partial x_j), \quad (74)$$

with $\delta_{ij}=1$ for $i=j$, $\delta_{ij}=0$ for $i\neq j$.

We shall also need the anisotropic formulation of the relation between the electrochemical potential gradient and the temperature gradient, the isotropic form of which can be gotten from (3), (19), and (X-7), namely,

$$\nabla\bar{\mu} = -e^2\rho \mathbf{J}^e - S^*\nabla T, \quad (75)$$

in which we have used the electrical resistivity $\rho = 1/\sigma$ instead of the conductivity. Equation (75) derives from the same basic relation (3) as does (73); that is, (73) was written as the anisotropic form of (72) or (21) which in turn was derived from (3). It is clear therefore that the anisotropic form of (75) must be consistent with (73) and (74), and a consideration of this question shows that the only uncertainty in the direct transcription of (75) to anisotropic form lies in the order of subscripts in the transport entropy matrix S_{ij}^*. Thus in (75) the question is, which of the following forms is the correct one consistent with (73) and (74),

$$\frac{\partial\bar{\mu}}{\partial x_i} = -e^2\rho_{ij}J_j^e - S_{ij}^*\frac{\partial T}{\partial x_j},$$

or (76)

$$\frac{\partial\bar{\mu}}{\partial x_i} = -e^2\rho_{ij}J_j^e - S_{ji}^*\frac{\partial T}{\partial x_j}?$$

The resistivity matrix $\rho_{ij}=\rho_{ji}$ and the thermal conductivity matrix $\kappa_{ij}=\kappa_{ji}$ are already known to be symmetric.[17] We shall show analytically that the *second form* in (76) is the correct one; however, it is helpful to consider first an intuitive argument for a two-dimensional case.

If the particle (electron) current densities J_1^e and J_2^e flow through an elemental cube inside the crystal at uniform temperature, with $\partial T/\partial x_j = 0$ we have from (73) for the entropy current densities

$$J_1^s = S_{11}^* J_1^e + S_{12}^* J_2^e, \quad (77)$$

$$J_2^s = S_{21}^* J_1^e + S_{22}^* J_2^e. \quad (78)$$

Next we suppose that a temperature gradient with components $\partial T/\partial x_1$ and $\partial T/\partial x_2$ but $\partial T/\partial x_3 = 0$ is established in the elemental cube and that no electrical or particle current is allowed to flow. From (75) we see that there will result a gradient of electrochemical potential. The question is, which of the following two sets of relations follows from (77) and (78):

$$\frac{\partial\bar{\mu}}{\partial x_1} = -S_{11}^*\frac{\partial T}{\partial x_1} - S_{12}^*\frac{\partial T}{\partial x_2}, \quad (A)$$

$$\frac{\partial\bar{\mu}}{\partial x_2} = -S_{21}^*\frac{\partial T}{\partial x_1} - S_{22}^*\frac{\partial T}{\partial x_2}, \quad (B)$$

or

$$\frac{\partial\bar{\mu}}{\partial x_1} = -S_{11}^*\frac{\partial T}{\partial x_1} - S_{21}^*\frac{\partial T}{\partial x_2}, \quad (79)$$

$$\frac{\partial\bar{\mu}}{\partial x_2} = -S_{12}^*\frac{\partial T}{\partial x_1} - S_{22}^*\frac{\partial T}{\partial x_2}? \quad (80)$$

Consider the significance of the "cross-term components" S_{12}^* and S_{21}^*. By (77), a particle current (density) J_2^e along axis x_2 contributes to the entropy current (density) J_1^s along axis x_1 through the component S_{12}^*. This means that particle currents along x_2 are coupled with entropy currents along x_1 through the components S_{12}^*. In the same way, by (78), particle currents along x_1 are coupled with entropy currents along x_2 through the component S_{21}^*. Equations (77) and (78) relate the currents or fluxes $\mathbf{J}^e$ and $\mathbf{J}^s$, while Eqs. (A) and (B) or (79) and (80) relate the "forces" $\nabla\bar{\mu}$ and ∇T. We saw in Sec. B that the flux $\mathbf{J}^e$ and the force $-\nabla\bar{\mu}$ are conjugate to each other, as are the flux $\mathbf{J}^s$ and the force $-\nabla T$. The present question in regard to the choice between (A) and (B) or (79) and (80) brings out the significance of the conjugation between fluxes and forces. This conjugation means that $\mathbf{J}^e$ and $-\nabla\bar{\mu}$ are related by what we may call a direct coupling, as are $\mathbf{J}^s$ and $-\nabla T$, whereas $\mathbf{J}^e$ (or $-\nabla\bar{\mu}$) is related to $\mathbf{J}^s$ (or $-\nabla T$) by an interference or indirect coupling. It will help to refer to $\mathbf{J}^e$ and $-\nabla\bar{\mu}$ as "electrical effects" and to $\mathbf{J}^s$ and $-\nabla T$ as "thermal effects." Thus, electrical effects along axis x_2 are connected by interference coupling with thermal effects along axis x_1 through the matrix component S_{12}^*, while electrical effects along axis x_1 are connected by interference coupling with thermal effects along axis x_2 through the matrix component S_{21}^*. If, from (77), J_2^e contributes to J_1^s through S_{12}^*, then we expect $\partial\bar{\mu}/\partial x_2$ to be related to $\partial T/\partial x_1$ through the same matrix component S_{12}^*; if, from (78) J_1^e contributes to J_2^s through S_{21}^*, we expect $\partial\bar{\mu}/\partial x_1$ to be related to $\partial T/\partial x_2$ through S_{21}^*. Therefore we recognize (79) and (80) as consistent with (77) and (78) and we reject (A) and (B).

To derive analytically the second of Eqs. (76) we make use of the conjugation of the fluxes and forces as expressed mathematically in the invariance (9) of the sum

$$\zeta(s) = J_i^e\left(-\frac{\partial\bar{\mu}}{\partial x_i}\right) + J_i^s\left(-\frac{\partial T}{\partial x_i}\right). \quad (81)$$

It was mentioned in connection with Eq. (9) that the time rate of internal entropy production per unit

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[17] See W. Voigt, *Lehrbuch der Kristallphysik*, p. 345, or de Groot, reference 2, Chapter 4. It has never been shown that for any arbitrary crystal symmetry the matrix S_{ij}^* is symmetric. The work of Kohler, to be discussed later, gives quantum-mechanical expressions for a matrix γ_{ij}, related to our S_{ij}^*, which are nonsymmetrical in the general case.

volume $\zeta(s)$ at temperature T is determined by the sum of products of conjugate currents and forces, as in (81). Since this rate of entropy production is independent of the choice of fluxes and forces, provided these are conjugate, the sum (81) is an invariant. (The total internal entropy production rate is of course the volume integral of (81) taken over the whole system.) For steady-state conditions, (81) is not only invariant with respect to transformations of fluxes and forces but is also constant in time, and as already mentioned in Sec. B, steady-state processes are the only ones we shall consider. We substitute (73) into (81) and find

$$\left.\begin{aligned} T\zeta(s) &= -J_i^e\frac{\partial\bar{\mu}}{\partial x_i}-J_i^s\frac{\partial T}{\partial x_i}=-J_i^e\frac{\partial\bar{\mu}}{\partial x_i} \\ &\qquad -S_{ij}{}^*J_j^e\frac{\partial T}{\partial x_i}+\frac{\kappa_{ij}}{T}\frac{\partial T}{\partial x_j}\frac{\partial T}{\partial x_i} \\ &= -J_i^e\left(\frac{\partial\bar{\mu}}{\partial x_i}+S_{ji}{}^*\right)\frac{\partial T}{\partial x_j}+\frac{\kappa_{ij}}{T}\frac{\partial T}{\partial x_j}\frac{\partial T}{\partial x_i}. \end{aligned}\right\} \tag{82}$$

We see that the terms in κ_{ij} account for the ordinary irreversible heat-conduction contribution to the entropy source strength. Likewise the terms in J_i^e account for the contributions from the irreversible Joule heating. In fact, the physical significance of the entropy source strength $\zeta(s)$ is that it represents the time rate of change, per unit volume, of the entropy produced by strictly irreversible effects within the volume. This quantity $\zeta(s)$ is required by the Onsager theory to be positive, though not every term in $\zeta(s)$ is individually required to be positive. Now the entropy of the material contained within a given volume ΔV is a constant in the steady state, since this entropy is a single-valued function of characteristic parameters of the material in ΔV such as the internal energy ΔU, number of particles ΔN, and the volume ΔV. The internal entropy production $\zeta(s)$ resulting from irreversible processes within ΔV is carried out by the vector $\mathbf{J}^s$ at a rate, div $\mathbf{J}^s$, just sufficient (in the steady state) to balance out $\zeta(s)$ so as to maintain a constant entropy within ΔV.

The Joule contribution to $T\zeta(s)$ can also be written

$$\rho_{ij}J_iJ_j=e^2\rho_{ij}J_i^eJ_j^e, \tag{83}$$

where $J_i=-eJ_i^e$ and $\rho_{ij}=\rho_{ji}$ is the resistivity matrix of the crystal at temperature T. Equating (83) to the Joule contribution in (82) we have

$$\begin{aligned} -J_i^e\left(\frac{\partial\bar{\mu}}{\partial x_i}+S_{ji}{}^*\frac{\partial T}{\partial x_j}\right) &\equiv e^2\rho_{ij}J_i^eJ_j^e \\ &= -J_i^e(-e^2\rho_{ij}J_j^e), \end{aligned} \tag{84}$$

and since the particle (electrical) current density components are independently variable, (84) gives

$$\frac{\partial\bar{\mu}}{\partial x_i}+S_{ji}{}^*\frac{\partial T}{\partial x_j}=-e^2\rho_{ij}J_j^e=e\rho_{ij}J_j, \tag{85}$$

or

$$\frac{\partial\bar{\mu}}{\partial x_i}=-e^2\rho_{ij}J_je-S_{ji}{}^*\frac{\partial T}{\partial x_j}, \tag{86}$$

which is the second form in (76).

It is interesting to notice that the Joule heat is not correctly given in general by E_iJ_j, with $E_i=-\partial\phi/\partial x_i$. In fact, we can show that this is so even in an isotropic homogeneous phase, as follows. The correct Joule heat expression is, when (83) and (85) are used,

$$\left.\begin{aligned} \rho J\cdot J &= \frac{1}{e}\left(\frac{\partial\bar{\mu}}{\partial x}+S^*\frac{\partial T}{\partial x}\right)\cdot J \\ &\qquad = \frac{1}{e}\left(\frac{\partial\mu}{\partial x}-e\frac{\partial\phi}{\partial x}+S^*\frac{\partial T}{\partial x}\right)\cdot J \\ &= \frac{1}{e}\left(\frac{\partial\mu}{\partial T}+S^*\right)\frac{\partial T}{\partial x}\cdot J+E\cdot J, \end{aligned}\right\} \tag{87}$$

where we have written $\partial\mu/\partial x=(\partial\mu/\partial T)(\partial T/\partial x)$ and $E=-\partial\phi/\partial x$. Thus we have $\rho J^2=E\cdot J$ only for a phase at uniform temperature, when $\partial T/\partial x=0$. This situation is analogous to that concerned with the generalized Ohm's law discussed in Example 4 of Appendix B.

2. Volume and Surface Heating Effects

The vector W_i in (74) gives the total energy current density at any point in the crystalline medium. In the steady state there can be no accumulation of energy within any infinitesimal volume element and the vector W_i must be divergenceless. Thus

$$\begin{aligned} \frac{\partial W_i}{\partial x_i}=0=T\frac{\partial(S_{ij}{}^*J_j^e)}{\partial x_i}+S_{ij}{}^*J_j^e\frac{\partial T}{\partial x_i}+\bar{\mu}\frac{\partial J_i^e}{\partial x_i} \\ +J_i^e\frac{\partial\bar{\mu}}{\partial x_i}-\frac{\partial}{\partial x_i}\left(\kappa_{ij}\frac{\partial T}{\partial x_j}\right). \end{aligned} \tag{88}$$

This relation and the following are thus valid for nonhomogeneous crystalline or crystalline-like media.[18] The third group of terms on the right-hand side of (88) vanish, since the particle current is divergenceless. Substitution of (86) into the fourth term on the right-hand side gives

$$\begin{aligned} J_i^e\frac{\partial\bar{\mu}}{\partial x_i} &= -e^2J_i^e\rho_{ij}J_j^e-J_i^eS_{ji}{}^*\frac{\partial T}{\partial x_j} \\ &= -e^2\rho_{ij}J_i^eJ_j^e-S_{ij}{}^*J_j^e\frac{\partial T}{\partial x_i}, \end{aligned} \tag{89}$$

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[18] An example of the latter kind of medium is a nonuniformly strained body in which the strains give rise to a crystalline-like anisotropy.

the last term here cancelling the second on the right-hand side of (88). Solving for the derivative $\partial(\kappa_{ij}\partial T/\partial x_j)/\partial x_i$ in (88) and writing $J_i^e = -(1/e)J_i$, where J_i is the electrical current density, we find

$$\frac{\partial}{\partial x_i}\left(\kappa_{ij}\frac{\partial T}{\partial x_j}\right) = -\rho_{ij}J_iJ_j - \frac{1}{e}T\cdot\frac{\partial(S_{ij}^*J_j)}{\partial x_i}. \tag{90}$$

Equation (90) is a general expression for the production of heat in an inhomogeneous, anisotropic medium, crystalline or otherwise.

In general the components S_{ij}^* of the transport entropy matrix depend on temperature and on position in an inhomogeneous medium, so that the derivatives of S_{ij}^* in (90) must include spatial as well as temperature variations. Thus, since in general $S_{ij}^* = S_{ij}^*(x_i, T)$, we must write

$$\frac{\partial S_{ij}^*}{\partial x_i} = \left(\frac{\partial S_{ij}^*}{\partial x_i}\right)_T + \left(\frac{\partial S_{ij}^*}{\partial T}\right)_{x_i}\cdot\frac{\partial T}{\partial x_i}, \tag{91}$$

and the last group of terms in (90) breaks down into the three groups

$$\begin{aligned} -\frac{T}{e}\frac{\partial(S_{ij}^*J_j)}{\partial x_i} = -\frac{T}{e}J_j\left(\frac{\partial S_{ij}^*}{\partial x_i}\right)_T \\ -\frac{T}{e}J_j\left(\frac{\partial S_{ij}^*}{\partial T}\right)_{x_i}\cdot\frac{\partial T}{\partial x_i} - \frac{T}{e}\frac{\partial J_j}{\partial x_i}. \end{aligned} \tag{92}$$

We shall use the following notation for the four separate groups of terms in (90) and (92):

$$\left.\begin{aligned} &\text{Joule:} && Q_J \equiv -\rho_{ij}J_iJ_j, && (93)\\ &\text{Peltier:} && Q_P \equiv -\frac{1}{e}TJ_j\left(\frac{\partial S_{ij}^*}{\partial x_i}\right)_T, && (94)\\ &\text{Thomson:} && Q_T \equiv -\frac{1}{e}TJ_j\left(\frac{\partial S_{ij}^*}{\partial T}\right)_{x_i}\cdot\frac{\partial T}{\partial x_i}, && (95)\\ &\text{Bridgman:} && Q_B \equiv -\frac{1}{e}TS_{ij}^*\frac{\partial J_j}{\partial x_i}. && (96) \end{aligned}\right\}\ \begin{array}{l}\text{(Volume}\\ \text{effects)}\end{array}$$

Each "Q" represents a heat absorbed per unit volume per unit time.[19] Our sign convention agrees with that of Bridgman,[20] absorbed heat being taken as positive. Ehrenfest and Rutgers[21] use the opposite convention. Equation (93) gives the Joule heat evolved and is therefore negative. If the medium is not homogeneous there is a volume Peltier heating effect Q_P given by (94).

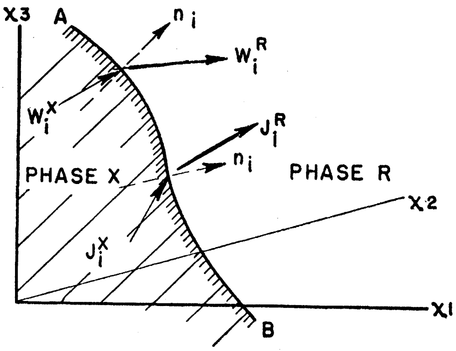

FIG. 11. The curve AB represents a general boundary between two anisotropic media X and R.

Whether the medium is homogeneous or not there is a Thomson heating effect given by (95). The signs in (93) and (95) agree with those in (58) and (59). The last terms (96) describe an effect first predicted by Bridgman.[22]

We consider next the phenomena taking place when an electrical current crosses a boundary between two anisotropic media. The generalization of the treatment in Sec. D follows directly from the formula (74) for total energy flow W_i. Consider a composite system consisting of two different anisotropic and inhomogeneous media X and R electrically and thermally jointed along some arbitrary surface AB as shown in Fig. 11. The reference axes are x_1, x_2, x_3 and the crystallographic axes (or other characteristic axes) of each medium X and R may be oriented in any way whatever relative to these reference axes. As in the case of isotropic media, the joint or contact AB between X and R will in general be a very complex transition region of some finite thickness d. This thickness is of course somewhat indefinite, varying from place to place along the boundary, and will depend upon the method used for joining the two media. Often the main bulk of the junction may consist primarily of some third material, for example when two different crystals are cemented together with Wood's metal or with soft solder. In such cases the junction layer of solder may be several thousandths of an inch thick in many places. On the other hand if the joining is done by electrical fusing of the two single crystals, the transition layer or sheath will probably be a physical mixture of polycrystals of X and R together with some alloy crystals, and so on. In almost all cases in which quantitative measurements are to be made on arbitrarily oriented single crystals the boundary AB will be a simple butt-joint as in Figs. 3, 5, and 28; in such cases some quantitative estimate can be made of the "contact resistance" or "sheath resistance" R_s provided the resistance matrices ρ_{ij}^X and ρ_{ij}^R for the two crystals X and R are known. The procedure for determining R_s in the case of two crystals

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[19] The electron charge e here, as throughout this Review, is the absolute value, the sign having been already absorbed in the original electrochemical potential separation into chemical and electrical portions.

[20] P. Bridgman, *Thermodynamics of Electrical Phenomena in Metals* (Macmillan Company, New York, 1934), Chap. VI.

[21] P. Ehrenfest and A. J. Rutgers, Proc. Acad. Sci. Amsterdam **32**, 698, 883 (1929).

[22] P. Bridgman, Proc. Am. Acad. Sci. **61**, 101 (1926); **63**, 351 (1929); Proc. Natl. Acad. Sci. **13**, 46 (1927).

is essentially the same as that already described in connection with Fig. 28 except for the added complications resulting from the crystalline nature of X and R. However, since these complications can be handled in a straightforward way having little to do with thermoelectricity, we shall not discuss the details.

Returning to formula (74) and Fig. 11 we see that since in the steady-state energy and charge cannot accumulate in the boundary region AB, the boundary conditions on total energy current density and electrical current density are

$$J_i^X n_i \equiv J_i^R n_i, \tag{97}$$

$$W_i^X n_i \equiv W_i^R n_i, \tag{98}$$

in which n_i are the three components of the unit normal vector which we agree always to point outward from medium X. The superscripts X and R refer to the medium in which the current flows. Applying the condition (98) to (74) and collecting similar terms for the two media we find

$$\frac{1}{e}T(S_{ij}^{*X}J_j^X n_i - S_{ij}^{*R}J_j^R n_i) + \frac{1}{e}(\bar{\mu}^X J_i^X n_i - \bar{\mu}^R J_i^R n_i) + \left[\kappa_{ij}^X\left(\frac{\partial T}{\partial x_j}\right)^X n_i - \kappa_{ij}^R\left(\frac{\partial T}{\partial x_j}\right)^R n_i\right] \equiv 0, \tag{99}$$

the generalized form of relation (37). The bracketted groups of terms represent the energy flowing out of the boundary region (per unit area of the sheath) by ordinary heat conduction through media X and R. The middle group of terms give the Joule dissipation in the resistance R_s of the sheath; this can be seen as follows. Writing $J_i = -eJ_i^e$ in (86), we have

$$\frac{\partial \bar{\mu}}{\partial x_i}\cdot n_i = e\rho_{ij}J_j\cdot n_i - S_{ji}^*\frac{\partial T}{\partial x_j}\cdot n_i.$$

Now the resistive sheath we assume to be isotropic, so that $\rho_{ij}=0$ for $i \neq j$, $\rho_{ii} \equiv \rho_s$; and if we further assume that the second term on the right-hand side of this last equation is negligible compared with the first, we find in crossing the boundary

$$\Delta\bar{\mu} \equiv \bar{\mu}^R - \bar{\mu}^X = \frac{\partial \bar{\mu}}{\partial x_i}\cdot n_i \cdot d = \left(\frac{\partial \bar{\mu}}{\partial s}\right)\cdot d \cong e\rho_s J_i n_i d, \tag{100}$$

where s is distance along the normal n_i and d is the thickness of the resistive sheath. Because of (97), it makes no difference which current components, J_i^X or J_i^R, are used in the last parentheses in (101), and we choose J_i^R. Then in the middle terms of (99), using (100) and (97) we get

$$\frac{1}{e}(\bar{\mu}^X J_i^X n_i - \bar{\mu}^R J_i^R n_i) = \frac{1}{e}(\bar{\mu}^X - \bar{\mu}^R)J_i^R n_i = \frac{1}{e}(-e\rho_s J_i^R n_i d)J_i^R n_i = -\rho_s d(J_i^R n_i)^2. \tag{101}$$

We can now rewrite (99):

$$\left[\kappa_{ij}^X\left(\frac{\partial T}{\partial x_j}\right)^X n_i - \kappa_{ij}^R\left(\frac{\partial T}{\partial x_j}\right)^R n_i\right] - \rho_s d(J_i^R n_i)^2 + \frac{1}{e}T(S_{ij}^{*X}J_j^X n_i - S_{ij}^{*R}J_j^R n_i) = 0. \tag{102}$$

Expression (102) describes the heat generation and transport at the boundary region between inhomogeneous, anisotropic media X and R, and is the surface analog of the "volume" equations (90). We name the second and third sets of terms as follows:

$$\left.\begin{aligned} &\text{Joule:} && q_J \equiv -\rho_s d(J_i n_i)^2, && (103)\\ &\text{Peltier:} && q_P \equiv \frac{1}{e}T(S_{ij}^{*X}J_j^X n_i - S_{ij}^{*R}J_j^R n_i). && (104)\end{aligned}\right\} \text{(Surface effects)}$$

Each of the "q" represents a heat absorbed per unit area per unit time.

We next set down the definitions

$$\Pi_{ij} \equiv \frac{1}{e}TS_{ij}^* \equiv \Pi_{ij}(T; x_1, x_2, x_3), \tag{105}$$

$$\tau_{ij} \equiv -\frac{1}{e}T\left(\frac{\partial S_{ij}^*}{\partial T}\right)_{x_i} \equiv \tau_{ij}(T; x_1, x_2, x_3). \tag{106}$$

We call Π_{ij} the Peltier coefficient matrix and τ_{ij} the Thomson coefficient matrix for a given inhomogeneous, anisotropic medium at temperature T and at point x_1, x_2, x_3 within the medium, when referred to rectangular coordinate axes x_1, x_2, x_3. Relations (93) through (96) for the volume heating effects become, with i, j $=1, 2, 3$,

$$\left.\begin{aligned} &\text{Joule:} && Q_J \equiv -\rho_{ij}J_i J_j, && (107)\\ &\text{Peltier:} && Q_P \equiv -\left(\frac{\partial \Pi_{ij}}{\partial x_i}\right)J_j, && (108)\\ &\text{Thomson:} && Q_T \equiv \tau_{ij}J_j\frac{\partial T}{\partial x_i}, && (109)\\ &\text{Bridgman:} && Q_B \equiv -\Pi_{ij}\frac{\partial J_j}{\partial x_i}; && (110)\end{aligned}\right\} \text{(Volume effects)}$$

and (103) and (104) for the surface heating effects become

$$\left.\begin{aligned} &\text{Joule:} && q_J \equiv -\rho_s d(J_i n_i)^2, && (111)\\ &\text{Peltier:} && q_P \equiv -(\Pi_{ij}^R J_j^R - \Pi_{ij}^X J_j^X)\cdot n_i. && (112)\end{aligned}\right\} \text{(Surface effects)}$$

3. Limitations Imposed on the Thermoelectric Matrix Components by Crystal Symmetry

For convenient reference we shall list in Table I the general schemes of matrix components for the entropy transport matrix S_{ij}^* for the six crystal systems. No proof has yet been given that the thermoelectric matrices must in general be symmetric; this is in contrast, for example, to the symmetric matrices $\rho_{ij}=\rho_{ji}$ and $\kappa_{ij}=\kappa_{ji}$. On the contrary, Kohler[23] has shown on the basis of a quantum-kinetic treatment that the thermoelectric matrices are not in general symmetric. On the other hand, all pure metals and metallic alloys that have been studied up to the present time are of such crystal symmetry that the matrix S_{ij}^* is not only symmetric but has components S_{I}^*, $S_{\text{II}}^*=S_{\text{I}}^*$, S_{III}^* in the principal-axes coordinate system.

TABLE I. The schemes of matrix components for the entropy transport matrix S_{ij}^* for the six crystal systems.

Triclinic			Monoclinic			Rhombic		
S_{11}^*	S_{12}^*	S_{13}^*	S_{11}^*	S_{12}^*	0	S_{11}^*	0	0
S_{21}^*	S_{22}^*	S_{23}^*	S_{21}^*	S_{22}^*	0	0	S_{22}^*	0
S_{31}^*	S_{32}^*	S_{33}^*	0	0	S_{33}^*	0	0	S_{33}^*
Tetragonal			Hexagonal			Cubic		
S_{11}^*	S_{12}^*	0	S_{11}^*	S_{12}^*	0	S_{11}^*	0	0
$-S_{12}^*$	S_{11}^*	0	$-S_{12}^*$	S_{11}^*	0	0	S_{11}^*	0
0	0	S_{33}^*	0	0	S_{33}^*	0	0	S_{11}^*

4. Thermoelectric Potential Differences in Rods Cut from Crystals for Which S_{ij}^* Becomes S_{I}^*, $S_{\text{II}}^*=S_{\text{I}}^*$, S_{III}^* in Principal-Axes System. The 1st Kelvin and Kohler Symmetry Relations

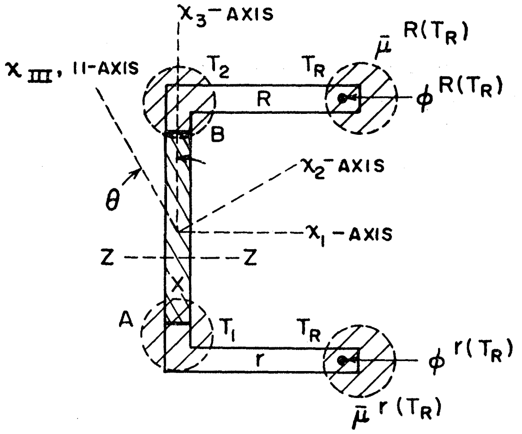

FIG. 12. The rod AB is cut from a crystal for which the transport entropy matrix S_{ij}^* becomes S_{I}^*, $S_{\text{II}}^*=S_{\text{I}}^*$, S_{III}^* in the principal-axes system. The angle between the ‖ axis of the crystal and the long axis of the rod is θ, as shown in Fig. 13.

The system we wish to analyze is the one shown in Fig. 12. The rod AB is cut from a single crystal of the material shown in Fig. 13. The slab $CDEF$ is in the $x_{\text{I}}-x_{\text{III}}$ plane, and for crystals with $S_{\text{II}}^*=S_{\text{I}}^*$ this is always the case when the ‖ axis is along x_{III}. We require here only that the final rod be oriented as shown with its long axis making an angle θ with the x_{III} or ‖ axis, and with this long axis lying in the $x_{\text{I}}-x_{\text{III}}$ plane. We then set up a new axis system x_1, x_2, x_3, with the x_2 axis coinciding with x_{II}, the x_1 and x_3 axes rotated (about x_2) through the angle θ as shown. The temperature gradient $\partial T/\partial x_3$ in Fig. 12 can be measured in principle by probing along a fixed axial line along the length of the rod AB. Also, from the known thermoelectric properties of the polycrystalline, homogeneous reference phase R it is easily possible to deduce the electrochemical potential difference $\bar{\mu}^{X(T_2)}-\bar{\mu}^{X(T_1)}$ between the ends of the crystalline rod AB once the difference $\phi^{R(T_R)}-\phi^{r(T_R)}=(1/e)(\bar{\mu}^{r(T_R)}-\bar{\mu}^{R(T_R)})$ has been measured potentiometrically, since no electrical current is supposed to flow through the crystal during this measurement. The electrochemical potential difference between the ends of the crystal rod is given by

$$\bar{\mu}^{X(T_2)}-\bar{\mu}^{X(T_1)}=\int_{T_1}^{T_2}(d\bar{\mu}^X/dT)dT$$

$$\equiv -\int_{T_1}^{T_2} S_{\text{eff}}^{*X}dT, \qquad (113)$$

in which S_{eff}^{*X} is defined by

$$\frac{\partial\bar{\mu}^X}{\partial x_3}=-S_{\text{eff}}^{*X}\frac{\partial T}{\partial x_3}, \qquad (114)$$

and is to be determined. By taking T_2-T_1 small, one can write

$$e(\phi^{r(T_R)}-\phi^{R(T_R)})=(S_R^*-S_{\text{eff}}^{*X})(T_2-T_1), \qquad (115)$$

using the procedure in Sec. C. From (115) one can thus determine $S_{\text{eff}}^{*X}=S_{\text{eff}}^{*X}(\theta)$, as a function of the angle θ between the ‖-principal axis and the long axis of the crystal rod, Figs. 12 and 13. The problem now is to determine the relationship between $S_{\text{eff}}^{*X}(\theta)$ and the

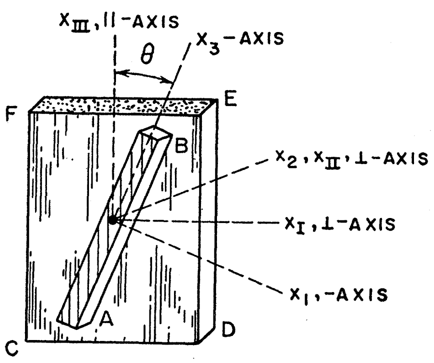

FIG. 13. The crystal rod AB of Fig. 12 is cut from the single-crystal slab $CDEF$, with orientation angle θ.

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[23] M. Kohler, Ann. Physik 27, 201 (1936).

principal values $S_{\parallel}^{*X}$ and $S_{\perp}^{*X}$ corresponding, respectively, to $\theta=0$ and $\theta=90°$. We shall show that the form of this relationship depends upon the boundary conditions used in the experiment for measuring S_{eff}^{*X}. To simplify the notation, however, we shall omit the superscript X, since it will be clear that we are now concerned only with the crystal rod and not with the reference phase R.

Let us first write out the complete expressions (74) and (86):

$$W_1=-\frac{1}{e}T(S_{11}^*J_1+S_{12}^*J_2+S_{13}^*J_3)-\frac{1}{e}\bar{\mu}J_1-\kappa_{11}\frac{\partial T}{\partial x_1}-\kappa_{12}\frac{\partial T}{\partial x_2}-\kappa_{13}\frac{\partial T}{\partial x_3},\tag{116}$$

$$W_2=-\frac{1}{e}T(S_{21}^*J_1+S_{22}^*J_2+S_{23}^*J_3)-\frac{1}{e}\bar{\mu}J_2-\kappa_{21}\frac{\partial T}{\partial x_1}-\kappa_{22}\frac{\partial T}{\partial x_2}-\kappa_{23}\frac{\partial T}{\partial x_3},\tag{117}$$

$$W_3=-\frac{1}{e}T(S_{31}^*J_1+S_{32}^*J_2+S_{33}^*J_3)-\frac{1}{e}\bar{\mu}J_3-\kappa_{31}\frac{\partial T}{\partial x_1}-\kappa_{32}\frac{\partial T}{\partial x_2}-\kappa_{33}\frac{\partial T}{\partial x_3},\tag{118}$$

$$\frac{\partial\bar{\mu}}{\partial x_1}=e(\rho_{11}J_1+\rho_{12}J_2+\rho_{13}J_3)-S_{11}^*\frac{\partial T}{\partial x_1}-S_{21}^*\frac{\partial T}{\partial x_2}-S_{31}^*\frac{\partial T}{\partial x_3},\tag{119}$$

$$\frac{\partial\bar{\mu}}{\partial x_2}=e(\rho_{21}J_1+\rho_{22}J_2+\rho_{23}J_3)-S_{12}^*\frac{\partial T}{\partial x_1}-S_{22}^*\frac{\partial T}{\partial x_2}-S_{32}^*\frac{\partial T}{\partial x_3},\tag{120}$$

$$\frac{\partial\bar{\mu}}{\partial x_3}=e(\rho_{31}J_1+\rho_{32}J_2+\rho_{33}J_3)-S_{13}^*\frac{\partial T}{\partial x_1}-S_{23}^*\frac{\partial T}{\partial x_2}-S_{33}^*\frac{\partial T}{\partial x_3}.\tag{121}$$

The components S_{ij}^* and κ_{ij} can be found in terms of the principal values S_{I}^*, $S_{\text{II}}^*=S_{\text{I}}^*$, S_{III}^* and κ_{I}, $\kappa_{\text{II}}=\kappa_{\text{I}}$, κ_{III} referred to principal axes by means of the usual formulas, namely,

$$S_{ij}^*=c_{li}c_{mj}S_{lm}^{*P},\quad \kappa_{ij}=c_{li}c_{mj}\kappa_{lm}^{P},\tag{122}$$

where the P superscript refers to principal-axes components, and c's are the direction cosines describing the transformation of axes as given by the following scheme:

$$\begin{array}{c|ccc} & x_1 & x_2 & x_3 \\ \hline x_{\text{I}} & c_{11} & c_{12} & c_{13} \\ x_{\text{II}} & c_{21} & c_{22} & c_{23} \\ x_{\text{III}} & c_{31} & c_{32} & c_{33} \end{array} = \begin{array}{c|ccc} & x_1 & x_2 & x_3 \\ \hline x_{\text{I}} & \cos\theta & 0 & \sin\theta \\ x_{\text{II}} & 0 & 1 & 0 \\ x_{\text{III}} & -\sin\theta & 0 & \cos\theta \end{array}\tag{123}$$

The direction cosines of the x_1 axis relative to x_{I}, x_{II}, x_{III} are, respectively, c_{11}, c_{21}, c_{31}, etc. Using (122) and (123) we find the matrices S_{ij}^* and κ_{ij} to be

$$\left\|\begin{matrix} S_{11}^* & S_{12}^* & S_{13}^* \\ S_{21}^* & S_{22}^* & S_{23}^* \\ S_{31}^* & S_{32}^* & S_{33}^* \end{matrix}\right\| = \left\|\begin{matrix} S_{\text{I}}^*\cos^2\theta+S_{\text{III}}^*\sin^2\theta & 0 & (S_{\text{I}}^*-S_{\text{III}}^*)\sin\theta\cos\theta \\ 0 & S_{\text{I}}^* & 0 \\ (S_{\text{I}}^*-S_{\text{III}}^*)\sin\theta\cos\theta & 0 & S_{\text{I}}^*\sin^2\theta+S_{\text{III}}^*\cos^2\theta \end{matrix}\right\|\tag{124}$$

and

$$\left\|\begin{matrix} \kappa_{11} & \kappa_{12} & \kappa_{13} \\ \kappa_{21} & \kappa_{22} & \kappa_{23} \\ \kappa_{31} & \kappa_{32} & \kappa_{33} \end{matrix}\right\| = \left\|\begin{matrix} \kappa_{\text{I}}\cos^2\theta+\kappa_{\text{III}}\sin^2\theta & 0 & (\kappa_{\text{I}}-\kappa_{\text{III}})\sin\theta\cos\theta \\ 0 & \kappa_{\text{I}} & 0 \\ (\kappa_{\text{I}}-\kappa_{\text{III}})\sin\theta\cos\theta & 0 & \kappa_{\text{I}}\sin^2\theta+\kappa_{\text{III}}\cos^2\theta \end{matrix}\right\|\tag{125}$$

The first set of boundary conditions represent the isothermal case, without electrical current, in which the lateral faces of the rod in Fig. 12 are supplied with or relieved of heat in such a way as to maintain these lateral faces at the same temperature at each level zz, though of course the temperature varies as one proceeds up the rod. In other words, the temperature-gradient components $\partial T/\partial x_1$ and $\partial T/\partial x_2$ are forced to vanish while the component up the length of the rod, $\partial T/\partial x_3$, is finite and in principle easily measurable. The isothermal conditions are therefore

$$J_1=J_2=J_3=\frac{\partial T}{\partial x_1}=\frac{\partial T}{\partial x_2}=0,\quad \frac{\partial T}{\partial x_3}=\frac{\partial T}{\partial x_3}.\tag{126}$$

Using these conditions in Eqs. (119), (120), (121), together with (124) and (114), we obtain the relations

$$\frac{\partial\bar{\mu}}{\partial x_1}=-S_{31}^*\frac{\partial T}{\partial x_3}=-S_{13}^*\frac{\partial T}{\partial x_3}=-(S_{\text{I}}^*-S_{\text{III}}^*)\sin\theta\cos\theta\frac{\partial T}{\partial x_3},\tag{127}$$

$$\frac{\partial\bar{\mu}}{\partial x_2}=-S_{23}^*\frac{\partial T}{\partial x_3}=0,\tag{128}$$

$$\frac{\partial\bar{\mu}}{\partial x_3}=-S_{33}^*\frac{\partial T}{\partial x_3}=-(S_{\text{I}}^*\sin^2\theta+S_{\text{III}}^*\cos^2\theta)\frac{\partial T}{\partial x_3}\equiv-S_{\text{eff}}^*\frac{\partial T}{\partial x_3}.\tag{129}$$

From (129) we deduce the important relation

$$S_{\text{eff}}^*(\theta)=S_{\text{I}}^*\sin^2\theta+S_{\text{III}}^*\cos^2\theta, \tag{130}$$

and after multiplying both sides by $(1/e)T$ and using (105) we find

$$\Pi_{\text{eff}}^{\text{isothermal}}(\theta)=\Pi_{\text{I}}\sin^2\theta+\Pi_{\text{III}}\cos^2\theta. \tag{131}$$

It is customary to set

$$\begin{gathered}S_{\text{I}}^*\equiv S_\perp^*,\quad S_{\text{III}}^*\equiv S_\parallel^*,\quad \Pi_{\text{I}}\equiv\Pi_\perp,\\ \Pi_{\text{III}}\equiv\Pi_\parallel,\quad \kappa_{\text{I}}\equiv\kappa_\perp,\quad \kappa_{\text{III}}\equiv\kappa_\parallel,\end{gathered} \tag{132}$$

so that (131) is written

$$\Pi_{\text{eff}}^{\text{isothermal}}(\theta)=\Pi_\perp\sin^2\theta+\Pi_\parallel\cos^2\theta. \tag{133}$$

Relation (133) was first derived by Kelvin[24] on the basis of intuitive reasoning, and is usually called the 1st Kelvin symmetry relation.

Turning next to the adiabatic case, we set up the conditions under which there is no lateral transfer of energy allowed across the side faces of the crystal rod; this is the case which most nearly approaches the usual experimental conditions. We allow electrical current $\mathbf{J}_3$ to flow in the x_3 direction in order to include complications arising from Peltier and Thomson effects. The adiabatic conditions then are

$$W_1=W_2=J_1=J_2=0,\quad W_3=W_3,\quad J_3=J_3. \tag{134}$$

Inserting conditions (134) into (116) through (121) we obtain

$$0=-\frac{1}{e}TS_{13}^*J_3-\kappa_{11}\frac{\partial T}{\partial x_1}-\kappa_{12}\frac{\partial T}{\partial x_2}-\kappa_{13}\frac{\partial T}{\partial x_3}, \tag{135}$$

$$0=-\frac{1}{e}TS_{23}^*J_3-\kappa_{21}\frac{\partial T}{\partial x_1}-\kappa_{22}\frac{\partial T}{\partial x_2}-\kappa_{23}\frac{\partial T}{\partial x_3}, \tag{136}$$

$$W_3=-\frac{1}{e}TS_{33}^*J_3-\frac{1}{e}\bar{\mu}J_3-\kappa_{31}\frac{\partial T}{\partial x_1}-\kappa_{32}\frac{\partial T}{\partial x_2}-\kappa_{33}\frac{\partial T}{\partial x_3}, \tag{137}$$

$$\frac{\partial\bar{\mu}}{\partial x_1}=e\rho_{13}J_3-S_{11}^*\frac{\partial T}{\partial x_1}-S_{21}^*\frac{\partial T}{\partial x_2}-S_{31}^*\frac{\partial T}{\partial x_3}, \tag{138}$$

$$\frac{\partial\bar{\mu}}{\partial x_2}=e\rho_{23}J_3-S_{12}^*\frac{\partial T}{\partial x_1}-S_{22}^*\frac{\partial T}{\partial x_2}-S_{32}^*\frac{\partial T}{\partial x_3}, \tag{139}$$

$$\frac{\partial\bar{\mu}}{\partial x_3}=e\rho_{33}J_3-S_{13}^*\frac{\partial T}{\partial x_1}-S_{23}^*\frac{\partial T}{\partial x_2}-S_{33}^*\frac{\partial T}{\partial x_3}. \tag{140}$$

First we wish to find the way in which S_{eff}^* depends on angle θ, thus giving the angular dependence of thermoelectric power; for this we set $J_3=0$, and we shall return afterwards to the Peltier and Thomson effects resulting from a nonvanishing J_3.

Therefore, after putting $J_3=0$ in (140), (135), and (136) we solve (135) and (136) for the two components $\partial T/\partial x_1$ and $\partial T/\partial x_2$ in terms of $\partial T/\partial x_3$. The solutions are

$$\begin{aligned}\frac{\partial T}{\partial x_1}&=\left(\frac{\kappa_{12}\kappa_{23}-\kappa_{22}\kappa_{13}}{\kappa_{11}\kappa_{22}-\kappa_{21}{}^2}\right)\frac{\partial T}{\partial x_3}\equiv\beta_1\frac{\partial T}{\partial x_3},\\ \frac{\partial T}{\partial x_2}&=\left(\frac{\kappa_{21}\kappa_{13}-\kappa_{11}\kappa_{23}}{\kappa_{22}\kappa_{11}-\kappa_{12}{}^2}\right)\frac{\partial T}{\partial x_3}\equiv\beta_2\frac{\partial T}{\partial x_3}.\end{aligned} \tag{141}$$

Substituting (141) into (140) with $J_3=0$ we find

$$\frac{\partial\bar{\mu}}{\partial x_3}=-(S_{13}^*\beta_1+S_{23}^*\beta_2+S_{33}^*)\frac{\partial T}{\partial x_3}. \tag{142}$$

Substituting the appropriate matrix components from (124) and (125) into (141) and (142) it is seen after some manipulation including the substitutions (132) and

$$-(1/e)S_\perp^*\equiv S_\perp^{\text{abs}},\quad -(1/e)S_\parallel^*\equiv S_\parallel^{\text{abs}}, \tag{143}$$

that (142) takes the form

$$\frac{\partial\bar{\mu}}{\partial x_3}=e\left[S_\perp^{\text{abs}}\sin^2\theta+S_\parallel^{\text{abs}}\cos^2\theta+\frac{(S_\parallel^{\text{abs}}-S_\perp^{\text{abs}})\left(\dfrac{\kappa_\perp}{\kappa_\parallel}-1\right)}{\sin^2\theta+\dfrac{\kappa_\perp}{\kappa_\parallel}\cos^2\theta}\sin^2\theta\cos^2\theta\right]\frac{\partial T}{\partial x_3}. \tag{144}$$

We shall call (144) the 1st Kelvin-Kohler symmetry relation, and one sees that multiplication of the bracketted term by T gives the relation

$$\Pi_{\text{eff}}^{\text{adiabatic}}(\theta)=\Pi_\perp\sin^2\theta+\Pi_\parallel\cos^2\theta+\frac{(\Pi_\parallel-\Pi_\perp)\left(\dfrac{\kappa_\perp}{\kappa_\parallel}-1\right)}{\sin^2\theta+\dfrac{\kappa_\perp}{\kappa_\parallel}\cos^2\theta}\sin^2\theta\cos^2\theta. \tag{145}$$

Comparison of (145) with (133) shows that deviations from the original Kelvin relation (133), in the case of adiabatically performed experiments, are to be expected if the thermal conductivity is highly anisotropic, so that $\kappa_\perp$ differs appreciably from $\kappa_\parallel$. This situation was clearly pointed out and (145) was derived first by

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[24] W. Thomson, Trans. Roy. Soc. Edinburgh **21**, 153 (1857).

Kohler,[25] although Stabler[26] and Reddemann[27] had previously realized that thermal conductivity played a role in the observed deviations from (133).

5. Transverse Effects in Rods Cut from Crystals for Which S_{ij}^* Becomes S_{I}^*, $S_{\mathrm{II}}^*=S_{\mathrm{I}}^*$, S_{III}^* in Principal-Axes System. The 2nd Kelvin and Kohler Symmetry Relation

From (127) it follows immediately upon multiplication by $-(1/e)T$ that under isothermal conditions

$$S^{\mathrm{abs}}_{\mathrm{transverse}}(\theta)=(S_{\perp}{}^{\mathrm{abs}}-S_{\parallel}{}^{\mathrm{abs}})\sin\theta\cos\theta, \tag{146}$$

which is the 2nd Kelvin symmetry relation; using (105) gives another form, namely,

$$\Pi^{\mathrm{abs}}_{\mathrm{transverse}}(\theta)=(\Pi_{\perp}-\Pi_{\parallel})\sin\theta\cos\theta. \tag{147}$$

A deeper insight into the physical meaning of (147) can be obtained from an alternate derivation of this relation. Suppose that the bar or rod in Fig. 12 is maintained isothermal throughout by the appropriate addition and removal (on opposite faces) of heat, and that an electrical current of uniform density J_3 is caused to flow through the rod, along the x_3 axis. The conditions to be maintained are therefore

$$\frac{\partial T}{\partial x_1}=\frac{\partial T}{\partial x_2}=\frac{\partial T}{\partial x_3}=J_1=J_2=0,\quad J_3=J_3. \tag{148}$$

Inserting these into the expressions (116) and (117) we find

$$W_1=-(1/e)TS_{13}{}^*J_3,\quad W_2=-(1/e)TS_{23}{}^*J_3. \tag{149}$$

Now W_1 and W_2 represent in this case the heat which must traverse the rod laterally, along the x_1 and x_2 directions, in order to maintain the zero temperature gradients, or isothermal conditions. These amounts of heat must be supplied and extracted on opposite faces of the rod. But from (124) it is seen that $S_{23}{}^*$ vanishes, and substitution of the appropriate component $S_{13}{}^*$ from (124) into W_1 in (149), followed by use of (105) and (132), gives again the relation (147).

If we set down the following adiabatic conditions, without electrical currents,

$$J_1=J_2=J_3=W_1=W_2=0,\quad W_3=W_3, \tag{150}$$

it can be shown that the resulting axial heat flow gives rise to a transverse electrochemical gradient $\partial\bar{\mu}/\partial x_1$ of amount

$$\left.\begin{aligned}\frac{\partial\bar{\mu}}{\partial x_1}&=-\left(S_{11}{}^*\frac{\partial T}{\partial x_1}+S_{21}{}^*\frac{\partial T}{\partial x_2}+S_{31}{}^*\frac{\partial T}{\partial x_3}\right)\\&=-(S_{11}{}^*\beta_1+S_{21}{}^*\beta_2+S_{31}{}^*)\frac{\partial T}{\partial x_3}\\&=-\left[(S_{\mathrm{I}}{}^*\cos^2\theta+S_{\mathrm{III}}{}^*\sin^2\theta)\frac{\left(\dfrac{\kappa_{\mathrm{I}}}{\kappa_{\mathrm{III}}}-1\right)}{\sin^2\theta+\dfrac{\kappa_{\mathrm{I}}}{\kappa_{\mathrm{III}}}\cos^2\theta}\right.\\&\qquad\left.+(S_{\mathrm{I}}{}^*-S_{\mathrm{III}}{}^*)\right]\sin\theta\cos\theta\frac{\partial T}{\partial x_3},\end{aligned}\right\} \tag{151}$$

and a transverse gradient $\partial\bar{\mu}/\partial x_2=0$. The latter result is to be expected from symmetry considerations. As before, it is seen that the adiabatic value (151) reduces to the isothermal value (127) when $\kappa_{\mathrm{I}}=\kappa_{\mathrm{III}}$.

The Thomson heat (per unit volume) for a specified current and temperature distribution can be found by using relations (109) and (106) together with (124), etc.

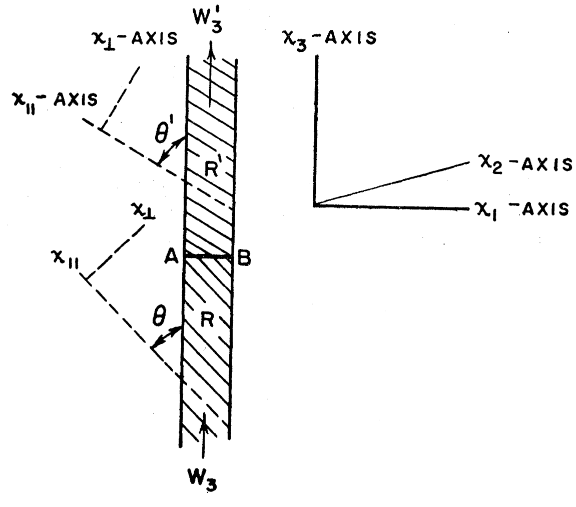

FIG. 14. The Peltier heat at junction AB between two rods cut from the same single-crystal slab depends on the orientation angles θ and θ' of the two rods. This Peltier heat, together with the Joule heat generated at the junction, is given by Eq. (152).

6. Bridgman Effect

Consider first a composite, rectangular cross section rod as shown in Fig. 14. The rod consists of two differently oriented rods R and R' whose long axes are oriented at angles θ and θ', respectively, with the $\parallel$ axis of a crystal with principal-axes components with $S_{\mathrm{I}}{}^*$, $S_{\mathrm{II}}{}^*=S_{\mathrm{I}}{}^*$, $S_{\mathrm{III}}{}^*$, and as before we set $S_{\mathrm{I}}{}^*=S_{\mathrm{II}}{}^*=S_{\perp}{}^*$, $S_{\mathrm{III}}{}^*=S_{\parallel}{}^*$. For isothermal boundary conditions, with $J_1=J_2=0$, $J_3\equiv J_0$, and $\partial T/\partial x_1=\partial T/\partial x_2=\partial T/\partial x_3=0$

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[25] M. Kohler, Ann. Physik 40, 196 (1941).
[26] H. P. Stabler, Phys. Rev. 46, 938 (1934).
[27] H. Reddemann, Ann. Physik 29, 286 (1937).

we can show from (116), (117), (118), and (124) that

$$\left.\begin{aligned}W_3'-W_3&=TJ_0^e[S_\perp^*(\sin^2\theta'-\sin^2\theta)\\&\quad+S_\parallel^*(\cos^2\theta'-\cos^2\theta)]-(1/A)i^2R_s,\\&=-(1/e)TJ_0(S_\perp^*-S_\parallel^*)\sin(\theta'+\theta)\\&\quad\times\sin(\theta'-\theta)-(1/A)i^2R_s,\end{aligned}\right\}\quad(152)$$

where W_3 is the total energy current density in rod R and W_3' is that in R', $J_0=-eJ_0^e$, $i=J_0A$, and A is the cross section area of the junction AB. The last term, in R_s (the "sheath" or "contact" resistance), comes from relation (X-17). Equation (152) gives the Peltier heat per unit area of the junction AB which must be supplied in order to maintain the junction temperature fixed after the electrical current is turned on. The heat generated at the junction by the Peltier effect is then the negative of (152). Consider next a "boomerang-shaped" specimen AB like that in Fig. 15, cut from a single crystal whose $\parallel$ axis is indicated by the vertical hatched lines. The lower portion is cut to make an angle θ with the $\parallel$ axis of the crystal, while the upper portion is cut to make the angle θ' with the $\parallel$ axis. The specimen is all one piece, so that there is no soldering or welding at the "junction" bc. We want to impose the following conditions on the specimens:

$$\frac{\partial T}{\partial x_1}=\frac{\partial T}{\partial x_1'}=\frac{\partial T}{\partial x_2}=\frac{\partial T}{\partial x_2'}=\frac{\partial T}{\partial x_3}=\frac{\partial T}{\partial x_3'}$$
$$=J_1=J_1'=J_2=J_2'=0,\quad J_3=J_3'\equiv J_0.\quad(153)$$

From (117) and (124) we find $W_2=W_2'=0$. The heat entering and leaving the sides of the lower and upper portions of the specimen, W_1 and W_1', respectively, are also found from (116) and (124):

$$W_1=-(1/e)T(S_\perp^*-S_\parallel^*)(\sin\theta\cos\theta)J_0,\quad(154)$$

$$W_1'=-(1/e)T(S_\perp^*-S_\parallel^*)(\sin\theta'\cos\theta')J_0.\quad(155)$$

The expressions give the heat entering (and leaving) per unit area through the lateral faces only at regions well away from the elbow of the specimen. In the immediate neighborhood of the elbow the situation is more complicated, as can be seen from the fact that the surface segments ab and $a'b$ have no counterpart on the opposite side of the elbow. In particular, the electrical current density distribution in the elbow region will be quite complicated, so that if we are to give a simple analysis of the effects in this region we shall be forced to idealize the situation in the following way. The electrical current density is assumed to be uniform in magnitude and direction throughout the lower region up to the line (plane) bc, at which plane it suddenly changes direction through the angle $\theta'-\theta$ to flow uniformly through the upper region of the specimen. In this case there is an "unbalanced" influx of heat of area density W_1 through the plane ab and another "unbalanced" influx of density W_1' through plane $a'b$. For a rectangular cross section of width b and of depth D perpendicular to the plane of the paper (Fig. 15), the areas ab and $a'b$ are $A=A'=Db\tan\frac{1}{2}(\theta'-\theta)$. According to (154) and (155) there will be in our idealized case a total influx of heat per unit time through ab and $a'b$ of amount

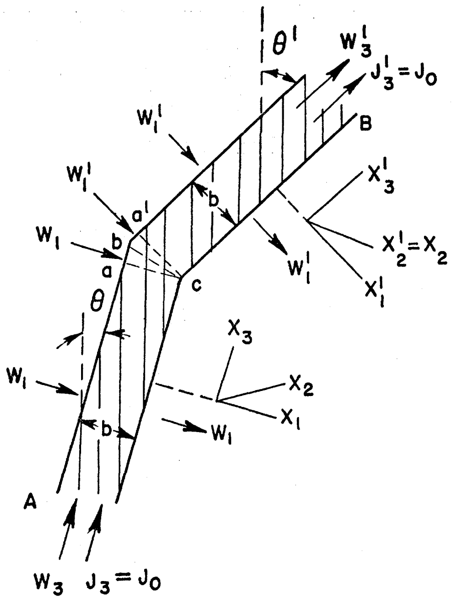

FIG. 15. The "internal Peltier heat" or "Bridgman heat" at the elbow of the single-crystal specimen AB is given by Eq. (160). This heating effect results from an uncompensated transverse flow of energy, as explained in the text.

$$\begin{aligned}W_1A+W_1'A'&=-(1/e)T(S_\perp^*-S_\parallel^*)(\sin\theta\cos\theta\\&\quad+\sin\theta'\cos\theta')J_0\cdot Db\tan\tfrac{1}{2}(\theta'-\theta).\quad(156)\end{aligned}$$

Furthermore, according to (152) there is a difference between W_3' and W_3 resulting from the fact that the electrical current density J_0 flows along different crystallographic directions in the upper and in the lower portions of the specimen AB in Fig. 15. However, the Joulean contribution is now not that resulting from a contact resistance R_s as in the case of Fig. 14, so that instead of the term in i^2R_s in (152) we must apply Eq. (107). The resistivity matrix is symmetrical and its components are exactly similar to those for κ_{ij} in Eq. (125) (or S_{ij}^* in (124)). For our idealized current distribution in Fig. 15 the total time rate of Joule heat generation in volume abc is thus simply the volume density (107) multiplied by the volume $\frac{1}{2}b^2D\tan\frac{1}{2}(\theta'-\theta)$, with a similar expression for the Joule heat in volume $a'bc$. The boundary conditions (153) give rise to only the single term $-\rho_{33}J_3$ in each region abc and $a'bc$. Using resistivity components similar to (124) and (125), together with notation corresponding to (132) we have

$$-\rho_{ij}J_iJ_j=-\rho_{33}J_3^2=-J_0^2(\rho_\perp\sin^2\theta+\rho_\parallel\cos^2\theta),\quad(157)$$

for volume *abc* and a corresponding expression for volume *a′bc*. The total heat added per unit time to the volume *aca′* is therefore the sum of (156) and the negative of *Db* times Eq. (152), with the expression

$$-(\rho_{33}J_3{}^2+\rho_{33}{}'J_3{}'^2)\cdot\tfrac{1}{2}b^2D\tan\tfrac{1}{2}(\theta'-\theta)$$
$$=-\tfrac{1}{2}b^2DJ_0{}^2[\rho_\perp(\sin^2\theta+\sin^2\theta')$$
$$+\rho_{\shortparallel}(\cos^2\theta+\cos^2\theta')]\tan\tfrac{1}{2}(\theta'-\theta),\quad(158)$$

substituted for $-(1/2A)(i^2R_s)$ in (152). The total heat added per unit time to *aca′* is thus

$$\left.\begin{aligned}Q=&+(1/e)TDbJ_0[S_\perp{}^*(\sin^2\theta'-\sin^2\theta)\\&+S_{\shortparallel}{}^*(\cos^2\theta'-\cos^2\theta)]-(1/e)TDbJ_0\\&\times(S_\perp{}^*-S_{\shortparallel}{}^*)(\sin\theta\cos\theta+\sin\theta'\cos\theta')\\&\times\tan\tfrac{1}{2}(\theta'-\theta)-\tfrac{1}{2}b^2DJ_0{}^2[\rho_\perp(\sin^2\theta+\sin^2\theta')\\&+\rho_{\shortparallel}(\cos^2\theta+\cos^2\theta')]\tan\tfrac{1}{2}(\theta'-\theta).\end{aligned}\right\}\quad(159)$$

Using the definition (105) in (159) and dividing by $(Db)J_0$, we find that the first two terms (without the Joule contribution) can be written

$$I(\theta,\theta')\equiv\Pi_\perp(\sin^2\theta'-\sin^2\theta)+\Pi_{\shortparallel}(\cos^2\theta'-\cos^2\theta)$$
$$+(\Pi_{\shortparallel}-\Pi_\perp)(\sin\theta\cos\theta+\sin\theta'\cos\theta')\tan\tfrac{1}{2}(\theta'-\theta).\quad(160)$$

Bridgman[20] calls the quantity $I(\theta,\theta')$ the "internal Peltier heat" and Eq. (160) is identical with his equation (VI-10). The existence of this internal Peltier effect was first pointed out by Bridgman. If specimen *AB* of Fig. 15 were cut along the planes *ac* and *a′c* and the two segments joined together again as in Fig. 14, the relation (160) is not valid unless we ignore the third term (containing $\tan\frac{1}{2}(\theta'-\theta)$); this is so even apart from the question of the Joule heat at the junction. Comparison of the results for Fig. 14 with those for Fig. 15 shows that they differ only by the last term in (160). One might say that an electron knows that in Fig. 15 it has not only changed its direction of motion relative to the crystal's axes, but that it has actually changed its direction of motion in space!

Finally, we discuss the general Bridgman terms (110) as applied to the crystal systems for which the matrix $S_{ij}{}^*$ can be reduced to principal values $S_{\mathrm{I}}{}^*=S_{\mathrm{II}}{}^*=S_\perp{}^*$ and $S_{\mathrm{III}}{}^*=S_{\shortparallel}{}^*$. We have

$$\left.\begin{aligned}-Q_B=&\Pi_{11}\frac{\partial J_1}{\partial x_1}+\Pi_{12}\frac{\partial J_2}{\partial x_1}+\Pi_{13}\frac{\partial J_3}{\partial x_1}\\&+\Pi_{21}\frac{\partial J_1}{\partial x_2}+\Pi_{22}\frac{\partial J_2}{\partial x_2}+\Pi_{23}\frac{\partial J_3}{\partial x_2}\\&+\Pi_{31}\frac{\partial J_1}{\partial x_3}+\Pi_{32}\frac{\partial J_2}{\partial x_3}+\Pi_{33}\frac{\partial J_3}{\partial x_3}.\end{aligned}\right\}\quad(161)$$

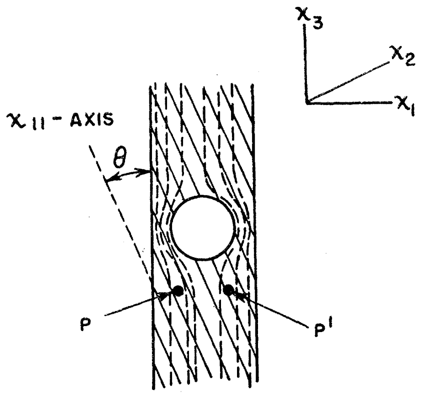

FIG. 16. The electrical current distribution in the ribbon, already asymmetric because of the anisotropy of resistivity, is made more complex as a result of the asymmetrical temperature distribution; this latter asymmetry is a consequence of the Bridgman heat term, Eq. (162).

As an example of the use of (161) we apply it to the situation in Fig. 16. The figure shows a long ribbon-shaped crystal cut with its long axis at an angle θ with the ‖ axis, and with a centrally located circular hole. The reference axes x_1, x_2, x_3 are oriented as shown in the figure. We have the conditions

$$J_2=\frac{\partial J_2}{\partial x_1}=\frac{\partial J_2}{\partial x_2}=\frac{\partial J_1}{\partial x_2}=\frac{\partial J_3}{\partial x_2}=\frac{\partial J_2}{\partial x_3}=0.$$

Inserting these conditions into (161) we find

$$-Q_B=\Pi_{11}\frac{\partial J_1}{\partial x_1}+\Pi_{13}\left(\frac{\partial J_3}{\partial x_1}+\frac{\partial J_1}{\partial x_3}\right)+\Pi_{33}\frac{\partial J_3}{\partial x_3},\quad(162)$$

where, for the crystals which concern us here, $\Pi_{13}=\Pi_{31}$. It would not be an easy problem to calculate the distribution of the electrical current density in this crystalline ribbon with a hole, but we can see nevertheless that the heating Q_B (per unit volume) is not symmetrical. This can be seen by a consideration of the signs of the various derivatives $\partial J_1/\partial x_1$, $\partial J_3/\partial x_1$, $\partial J_1/\partial x_3$, $\partial J_3/\partial x_3$ at two geometrically opposite points *P* and *P′*. Thus the Bridgman heat Q_B leads to a nonsymmetric temperature distribution if current is passed through the ribbon.

If the crystal is cubic so that $S_{\shortparallel}{}^*=S_\perp{}^*$, $\Pi_\perp=\Pi_{\shortparallel}$, it follows from (124) that $S_{13}{}^*$ and Π_{13} vanish, and $\Pi_{\shortparallel}=\Pi_\perp=\Pi_{33}=\Pi_{11}$. Because of the divergenceless nature of the electrical current density, $\partial J_1/\partial x_1+\partial J_3/\partial x_3=0$ and the Bridgman heat Q_B in (162) vanishes. In the same way, if $\Pi_{\shortparallel}=\Pi_\perp$, the "internal Peltier heat" (160) vanishes. Cubic crystals are thermoelectrically isotropic.

A curious and interesting consequence of the Bridgman effect is illustrated in Fig. 17. Suppose that a long, thin, noncubic single crystal is either carefully bent or else grown in the shape of an arc as shown in the figure. If an electrical current is passed through the bent crystal rod the current density will not be quite uniform. But let us assume that the density is nearly uniform and of value $J_3 = J_0$. The angle between current and crystal axis is the same throughout the length of the crystal. As shown by the short arrows, there will be in the isothermal state a heat flow density W_1 into one side and, if the rod were straight, an equal flow density out the opposite side. But if the rod is bent, the outer surface AA' is larger than the inner surface BB' and the temperature distribution must now change. Thus, although the electron "sees" the same axis orientation as it proceeds around the bend, the particle seems to "know" that it is changing its direction relative to some fixed external reference system.

7. Kelvin Thermoelectric Relations in Anisotropic Media

In our formulation of the theory, the Kelvin thermoelectric relations seem almost trivial. From the definitions (105) and (106), together with the definition

$$S_{ij}^{\text{abs}} \equiv -(1/e)S_{ij}^*, \tag{163}$$

it follows immediately that

$$\Pi_{ij} = -TS_{ij}^{\text{abs}}, \tag{164}$$

and

$$\tau_{ij} = T\left(\frac{\partial S_{ij}^{\text{abs}}}{\partial T}\right)_{x_i}; \tag{165}$$

for a homogeneous crystalline or anisotropic medium the x_i subscript is superfluous.

8. Comparison with Treatments of Kelvin, Bridgman, Ehrenfest and Rutgers, Kohler, Meixner, and Meissner

Meissner[14] in his treatment of thermoelectric anisotropy considers only the reversible effects of thermoelectricity, and begins by assuming that heat is generated (reversibly) by an electrical current, first as a result of a temperature gradient (Thomson effect), second by a change of direction of the current (Bridgman effect), and third at the boundary between two substances (Peltier effect). He postulates a tensor relation for these reversible effects, this relation containing *a priori* the three terms corresponding to the Thomson, Bridgman, and Peltier heats and containing certain as yet undefined tensor components. By applying the resulting equations to particular cases of crystalline rods Meissner deduces relationships between these tensor components. The theory is then applied to derive the Kelvin symmetry relations.

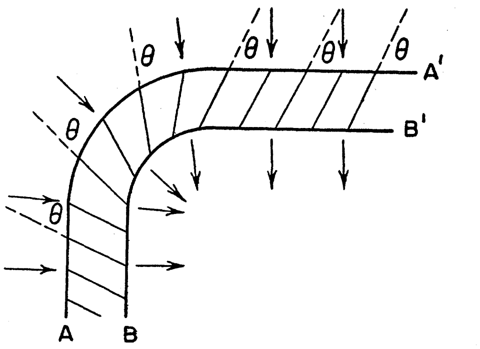

FIG. 17. The Bridgman effect gives rise to a distortion in the original temperature distribution in the curved single-crystal when an electrical current is passed through the crystal. This alteration in the temperature distribution is superposed in a complicated way upon that caused by Joule heating.

Kohler[23,25] develops a general quantum-kinetic theory for metals of arbitrary crystal form, first setting up transport integrals suitable for anisotropic electron scattering. The electrical and heat current densities are then expressed in terms of these transport integrals. By next setting up "flow" equations analogous to our Eqs. (4) and (5), with now an electrical potential gradient and a temperature gradient as generalized forces, Kohler introduces tensor components γ_{ij} (analogous to our S_{ij}^*) which are expressed in terms of the transport integrals. In this way he has shown that only for simplifying assumptions about the electron scattering does the tensor γ_{ij} become symmetric.

Kohler finds the Ehrenfest-Rutgers relations for the reversible heat generation and an expression for what he calls the "thermoelectric field intensity" F_i^{th}, given by Eq. (21) of his 1936 paper:

$$F_i^{\text{th}} = \sum_{j=1}^{3} S_{ij}\frac{\partial T}{\partial x_j} - \frac{\partial R}{\partial x_i} \equiv S_{ij}\frac{\partial T}{\partial x_j} - \frac{\partial R}{\partial x_i} \tag{166}$$

in our repeated-index notation. Let us rewrite our Eq. (86) in terms of current density J_i and of chemical and electrical potential; also, let us write $-(1/e)S_{ij}^* \equiv S_{ij}^{\text{abs}}$ and group the terms as follows:

$$-\frac{\partial \phi}{\partial x_i} - \rho_{ij}J_j = S_{ji}^{\text{abs}}\frac{\partial T}{\partial x_j} - \frac{1}{e}\frac{\partial \mu}{\partial x_i}. \tag{167}$$

Comparison of (167) with (166) allows us to connect our results with those of Kohler. First, it is seen that Kohler's "thermoelectric field intensity" F_i^{th} corresponds to our "homogeneous thermoelectric potential gradient" as defined in Example 3 of Appendix B. Kohler's F_i^{th} is thus the gradient of the electrical potential resulting from a temperature gradient after the $\rho_{ij}J_j$ terms have been subtracted. His quantity R is simply $-(1/e)$ times the chemical potential. Secondly, his S_{ij} corresponds to our S_{ji}^{abs}, the absolute thermopower tensor. In Kohler's flow equations this tensor appears with indices reversed, S_{ji}, in agreement with the situation we discussed in the derivation of our Eq. (86). The fact that our indices and those of Kohler are the reverse of each other throughout is of course trivial. When the time arrives that numerical data are tabulated for very low-symmetry crystals, it will be necessary to decide whether a given matrix component should be called S_{13}^* or S_{31}^*, for example.

In his 1941 paper Kohler gives an excellent discussion of the assumptions upon which the Kelvin symmetry relations are derived and shows how different experimental boundary conditions lead to more complicated expressions. We have already derived these expressions and discussed their significance.

Meixner[28] gives both a thermodynamic and a kinetic treatment of thermoelectric effects and discusses thermoelectric phenomena in a magnetic field. His treatment quite closely parallels the present treatment in the forms of the equations, except of course that his theory is not based on the Onsager-Callen-de Groot method. One of Meixner's energy flow equations, for example, can be shown to be identical with our Eq. (74) for W_i, except for the discrepancy that his contains a term ζJ_j instead of our $\bar{\mu} J_j$. The quantity ζ Meixner calls the "thermodynamic potential per electron," which is equivalent to our μ or chemical potential per particle.[29] Furthermore, he obtains an equation for the field intensity $-\partial\phi/\partial x_i$ which is exactly identical with our (86) when $\bar{\mu}$ is separated into chemical and electrical parts and J_j is used instead of J_j^e.

Ehrenfest and Rutgers[21] begin by postulating the general anisotropic form (92) for the reversible thermoelectric effects, and their formulation was the first to include the Bridgman effect. Irreversible effects were excluded in their analysis.

Kelvin[24] derived his symmetry relations on the basis of intuitive arguments involving the additivity of Peltier heats resulting from the separate components of the electric current density vector, and he later generalized his arguments using heat-flow and "emf" equations in terms of certain matrix components. However, his treatment was not sufficiently general to include the Bridgman effect. Bridgman,[22] also on the basis of certain intuitive arguments well described in his book,[20] concluded that an electrical current passing through a corner of a noncubic crystal should absorb or give out heat in the form of an "internal Peltier heat." We have already discussed this effect, and reference is made to Bridgman's book. The quantity R used by Bridgman and by Ehrenfest and Rutgers corresponds to our chemical potential μ.

H. EFFECTS OF CHEMICAL AND PHYSICAL INHOMOGENEITIES IN AN ISOTROPIC MEDIUM

We have seen in Sec. C that the thermoelectric potential difference for a thermocouple consisting of two homogeneous, isotropic phases depends only on the temperatures of the two junctions. In particular, if these two temperatures are the same, there will be a zero thermoelectric potential difference. This empirical rule is known as Magnus' law.[11] This is no longer true, and the law of Magnus is no longer valid, if either or both of the wires composing the thermocouple are not chemically and physically homogeneous. We shall not discuss the ways in which cold work, impurities, stress and other irregularities affect the thermopower of a material.[30] We wish only to give a short formula to show that the electrical potential difference of a thermocouple measured by a potentiometer depends upon the temperature distribution along the wires in case the wires are not homogeneous. Let us suppose that the reference material R indicated in Fig. 18 is homogenous while the wire X is not. From Eq. (27) we see that the contribution to $\phi^r-\phi^R$ from the wires R vanishes when the upper ends of both are at T while the lower ends are at T_R as indicated in the figure. On the other hand, for the contribution from X we have, using (27) and (X-10),

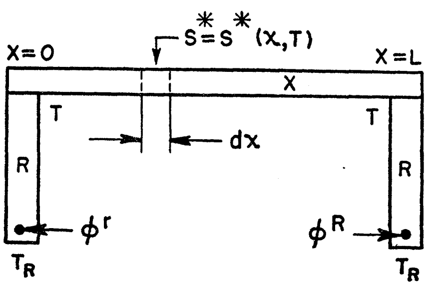

FIG. 18. The electrical potential difference $\phi^r-\phi^R$ depends on the temperature gradients in wire X when this latter wire is chemically inhomogeneous.

$$e(\phi^r-\phi^R)=\int_0^L (d\bar{\mu}/dx)dx = -\int_0^L S^*(x,T)(dT/dx)dx, \quad (168)$$

since in the inhomogeneous wire X the quantity S^* depends on both the position in the wire and the temperature at this point. If X were homogeneous we should have $S^*=S^*(T)$ only and the integral (168) would vanish, in accordance with the law of Magnus. But for an inhomogeneous wire it is clear that (168) does not in general vanish even when the ends are at the same temperature. In fact, a simple test of homogeneity in a wire consists of measuring the potential difference across a thermocouple made with the wire, when the ends are fixed in ice water, say, and the central portion of the wire is held against a block of solid CO_2 or passed through a pool of liquid nitrogen.

I. ON THE THERMOELECTRIC EFFECTS OF BENEDICKS

It was seen in Sec. H that thermocouples made of chemically and physically homogeneous phases obey the law of Magnus, at least according to the theory of irreversible processes as discussed here. We have also seen that the thermopower of a metal depends upon

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[28] J. Meixner, Ann. Physik **35**, 701 (1939); **40**, 165 (1941).

[29] Meixner's electron charge e is negative.

[30] A. W. Sáenz, Phys. Rev. **91**, 1142 (1953).

crystallographic orientation when the metal is anisotropic either crystallographically or because of strains, etc. From Sec. H, then, it is clear that a wire which consists of fairly large crystallites might actually not obey Magnus' law. There have been numerous attempts to show that Magnus' law does not hold even if the wires are perfectly homogeneous both chemically and physically, and the most serious of these attempts were those of Benedicks and his co-workers.[31] Many other workers have attempted to repeat the findings of Benedicks but almost all have shown that upon careful annealing and homogenization of their samples, the law of Magnus remained valid and the Benedicks effects were eliminated.[32]

In order to include the reported Benedicks effects in our theory it would not be sufficient simply to allow the parameters S_{ij}^* to depend on the temperature gradient as well as on the temperature itself. In fact, the theory would need to be extended to a higher approximation, since the thermodynamics of Onsager *et al.* is based on the assumption that a temperature, entropy density, etc., can be assigned to each point in a continuous medium. This assumption appears to be valid if the energy distribution function of the particles involved in a problem is not too greatly disturbed by temperature gradients and electrical current flows, for example. At least in the case of metals it is found that Ohm's law and Fourier's law are very accurately valid for all practically accessible current densities and temperature gradients. One might say that it does not seem to be possible experimentally to create enormous "turbulence" in the electron gas in a metal; the most violent electrical or thermal treatment applied to a metal in the laboratory creates only an extremely mild perturbation on the motion of the electrons inside the metal. It would seem to be quite safe to say, therefore, that, although a significant disturbance of the metallic-electron distribution function would cause deviations from the theory which we have outlined here and although such deviations might very well introduce electrical effects dependent on temperature gradients as well as on temperature as required for the Benedicks effects, it appears extremely unlikely that such a situation arises under ordinary circumstances with ordinary metals. In any case the effects reported by Benedicks and his co-workers seem to be very small and not particularly reproducible, so that until more affirmative evidence is produced we shall not deal with these reported effects any further.

The writer wishes to thank Dr. Conyers Herring for reading a large portion of this Review and for his friendly and constructive criticism. He is also greatly indebted to Mr. Erik Klokholm and to Dr. D. P. Detwiler for numerous helpful discussions. To Dr. F. C. Nix the writer extends his sincere thanks for his continued interest and encouragement. It is also a pleasure to acknowledge the financial support furnished by the Squier Signal Laboratories, Fort Monmouth, New Jersey, and in particular to mention the valuable encouragement given by Mr. George Hunrath of the Squier Laboratories.

APPENDIX A. ELEMENTARY EXAMPLES OF SEPARATION OF ELECTROCHEMICAL POTENTIAL

Example a.—Consider a single homogeneous phase of a certain atomic species, and for definiteness let it be, say, one kilogram of pure copper. The total Gibbs energy G is of course an extensive parameter, so that in the case of a single phase the Gibbs energy per atom is identical with the partial derivative $(\partial G/\partial N)$, where N is the total number of neutral copper atoms in the kilogram of copper. This quantity $(\partial G/\partial N)_{P,T}=G/N \equiv \mu_{\mathrm{Cu}^0}$ in this case (since the neutral atom has zero charge) is just the chemical potential of a neutral copper atom in the pure copper phase (at the particular P and T in question). It can be shown from thermostatics that if we imagine the copper ions Cu^{++} to "react" with the conduction or "free electrons" of charge $-e$ (e positive) in the lattice, according to the "reaction"

$$\mathrm{Cu}^{++}+2e\rightleftharpoons\mathrm{Cu}^0, \tag{X-1}$$

then the electrochemical potentials $\bar{\mu}_{\mathrm{Cu}^{++}}$, $\bar{\mu}_{-e}$ and $\bar{\mu}_{\mathrm{Cu}^0}$, must at equilibrium satisfy the relation

$$\bar{\mu}_{\mathrm{Cu}^{++}}+2\bar{\mu}_{-e}=\bar{\mu}_{\mathrm{Cu}^0}. \tag{X-2}$$

Here $\bar{\mu}_{\mathrm{Cu}^{++}}$ is the electrochemical potential of the ion Cu^{++} in the solid copper phase at a particular temperature and pressure, and similarly $\bar{\mu}_{-e}$ is the electrochemical potential of an electron in the copper. However, for an uncharged component, the electrochemical potential is identical with the chemical potential, and so $\bar{\mu}_{\mathrm{Cu}^0}=\mu_{\mathrm{Cu}^0}$. The values of the chemical potential μ_{Cu^0} are easy enough to obtain in principle from straightforward electrical-calorimetric measurements and the relation $G=H-TS$. If H is the enthalpy of the kilogram of copper and S its entropy at temperature T, then $dH=TdS+VdP$ and if the calorimetric measurements are done at constant pressure, $dH=TdS=dQ=$ (electrical power input)$\times$(time). From this we get the dependence of H on T (except for an arbitrary constant), and also $C_P=(\partial H/\partial T)_P$. The entropy S is

$$\int_{T_0}^{T}(C_P/T)dT=\int_{T_0}^{T}(\partial H/\partial T)(dT/T),$$

where T_0 is the temperature at the arbitrary "standard state" at which $H=0$ by definition. Finally, substituting the numerical values into $G=H-TS$ and $G/N=\mu_{\mathrm{Cu}^0}$, we get the desired numerical values of the chemical potential μ_{Cu^0} of a neutral copper atom in the solid copper phase as well as the dependence on the temperature.

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[31] C. Benedicks, Ann. Physik **55**, 1 (1918); **55**, 103 (1918); C. Benedicks and G. Siljeholm, Arkiv Mat., Astron. Fys. **23A**, Nr. 27; **24A**, Nr. 1 and Nr. 7 (1933).

[32] N. Fuschillo, Proc. Phys. Soc. (London) **B65**, 896 (1952).

Example b.—Now let us suppose that the kilogram of copper is in the form of a sphere and is always kept at constant temperature and pressure in vacuum.[33] We place a charge of approximately 10 microcoulombs on the sphere (of radius approximately 0.03 meter for 1 kg of copper). Ten microcoulombs of electrons represent about 10^{-5} mole (Faraday) of electrons and this charge would therefore change the weight of the sphere by roughly 5×10^{-14} g or 5×10^{-15} percent of the sphere's original weight. This minute change can hardly be expected to affect the chemical properties of the copper. Yet if we calculate the change in the electrostatic potential ϕ of the sphere when the 10 microcoulombs are added, we find a change of about 3 million volts. Certainly it seems safe in this case to state that the chemical potential of an electron on the sphere has been completely unaffected by the addition of the charge whereas the electrical potential has been very greatly changed. The change in the electrochemical potential $\bar{\mu}_{-e}{}^{\mathrm{Cu}}$ of an electron on the copper sphere is thus simply the change $-e\phi$, where $-e$ is the electronic charge in coulombs and ϕ is the change in electrical potential inside the metal, in volts, while the chemical potential $\mu_{-e}{}^{\mathrm{Cu}}$ has remained unchanged.

Let us compare the results of the two examples. We write Eq. (X-2) in terms of chemical potentials and electrical potentials:

$$\bar{\mu}_{\mathrm{Cu}^{++}}=\mu_{\mathrm{Cu}^{++}}+2e\phi, \tag{X-3}$$

$$2\bar{\mu}_{-e}=2\mu_{-e}-2e\phi, \tag{X-4}$$

and by substitution of (X-3) and (X-4) in (X-2) we get

$$\begin{aligned}\bar{\mu}_{\mathrm{Cu}^0}&=\mu_{\mathrm{Cu}^{++}}+2e\phi+2\mu_{-e}-2e\phi\\&=\mu_{\mathrm{Cu}^{++}}+2\mu_{-e}=\mu_{\mathrm{Cu}^0},\end{aligned} \tag{X-5}$$

the electrical terms cancelling out as they should, since Cu^0 is uncharged and $\bar{\mu}_{\mathrm{Cu}^0}$ must be identical with μ_{Cu^0}. We have been able to measure $\bar{\mu}_{\mathrm{Cu}^0}$ or its equivalent μ_{Cu^0} and we have calculated ϕ, but we have not been able to deduce from these quantities alone the value of $\mu_{\mathrm{Cu}^{++}}$ nor of μ_{-e}, so that we are unable to assign numbers to the formal separation of $\bar{\mu}_{\mathrm{Cu}^0}$ into the parts $\bar{\mu}_{\mathrm{Cu}^{++}}$ and $2\bar{\mu}_{-e}$. Similarly, in Eqs. (X-3) and (X-4) we know only ϕ and have not been able therefrom to deduce values of $\mu_{\mathrm{Cu}^{++}}$, μ_{-e}, $\bar{\mu}_{\mathrm{Cu}^{++}}$, or $\bar{\mu}_{-e}$. It is possible in principle to calculate μ_{-e}, for example, and using Eq. (X-4), then (X-2), we can compute $\bar{\mu}_{\mathrm{Cu}^{++}}$ and from (X-3) we finally get $\mu_{\mathrm{Cu}^{++}}$, so that all parameters in (X-2), (X-3), and (X-4) will have been determined. The calculation of μ_{-e} must be based on a specific model, such as the "free-electron gas"[34] for instance; hence if the model is a poor one the value deduced for $\mu_{\mathrm{Cu}^{++}}$ will be wrong.

APPENDIX B. APPLICATIONS OF THE THEORY TO SPECIAL SYSTEMS

Example 1. Isothermal Electrical Conduction in a Single Homogeneous Phase

Writing $\mathbf{J}=-e\mathbf{J}_e$ for the electrical current density and using (3) we have

$$\mathbf{J}=eL_{ee}\nabla\bar{\mu}=eL_{ee}(\nabla\mu-e\nabla\phi)=-e^2L_{ee}\nabla\phi, \tag{X-6}$$

since the chemical potential is uniform throughout the homogeneous phase when the phase is isothermal. The electrical field intensity $\mathbf{E}$ inside the phase is minus the gradient of the electrical potential, so that we can write

$$\mathbf{J}=e^2L_{ee}\mathbf{E}\equiv\sigma\mathbf{E},$$

which is Ohm's law with σ representing the temperature-dependent isothermal electrical conductivity. This gives us an easy way to measure the coefficient L_{ee}, namely,

$$L_{ee}\equiv\sigma/e^2. \tag{X-7}$$

In Fig. 1, if R_{AB} is the total electrical resistance (at uniform temperature) of the cylinder (wire) between cross sections A and B and i is the total uniform electrical current in the wire, then Eq. (X-6) can be written

$$\phi^{X(T)}(B)-\phi^{X(T)}(A)=\Delta\phi^{X(T)}=iR_{AB},$$

where $\phi^{X(T)}(B)-\phi^{X(T)}(A)$ is the difference in electrical potential between sections A and B. This relation, Ohm's law, will be used in Appendix C in discussing the principle of the Poggendorf potentiometric method for measuring electrical potential differences between two separate wires of the same phase (not necessarily identical with phase X) and at the same temperature.

Example 2. Heat Conductivity without Electrical Current

From (8) we see that $(\mathbf{J}_q)_{\mathbf{J}_e=0}=T(\mathbf{J}_s)_{\mathbf{J}_e=0}$ when $\mathbf{J}_e=0$, so that with (21) we find for the heat flow $(\mathbf{J}_q)_{\mathbf{J}_e=0}$

$$\begin{aligned}(\mathbf{J}_q)_{\mathbf{J}_e=0}&=T(\mathbf{J}_s)_{\mathbf{J}_e=0}\\&=(T/L_{ee})(L_{es}{}^2-L_{ee}L_{ss})\nabla T\equiv-\kappa\nabla T,\end{aligned}$$

where κ is the thermal conductivity for zero electrical current. Therefore

$$\kappa\equiv(T/L_{ee})(L_{ee}L_{ss}-L_{es}{}^2), \tag{X-8}$$

giving the ordinary thermal conductivity in terms of the "L" phenomenological coefficients. From (22) we find directly

$$\kappa\equiv(1/TM_{ee})(M_{ee}M_{qq}-M_{eq}{}^2), \tag{X-9}$$

the ordinary thermal conductivity expressed in terms of the "M" coefficients. From (X-8) and (X-9), with (16) and (17) we can again find after some manipulation the expression (18).

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[33] This illustration is given by E. A. Guggenheim, on p. 331 of reference 3.

[34] The quantity μ_{-e} for an ideal free-electron gas in a metal is given, e.g., by Eq. (5.6), page 81 of Slater's *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939). It is generally called the Fermi energy parameter in the Fermi-Dirac distribution function.

Example 3. Electrical Potential Gradient in a Homogeneous Phase with Temperature Gradient but no Electrical Current

In this example we consider the practicability of determining the electrical potential gradient $\nabla\phi^{X(T)}$ in a single homogeneous chemical phase X when there exists a temperature gradient ∇T but no current flow. Setting $\mathbf{J}_e=0$ in Eq. (3) and separating the electrochemical potential into chemical and electrical parts, we have

$$\nabla\bar{\mu}^{X(T)}=-(L_{es}/L_{ee})\nabla T$$
$$=-S_X^*\nabla T=\nabla\mu^{X(T)}-e\nabla\phi^{X(T)}. \quad \text{(X-10)}$$

The electrical potential gradient is then

$$\nabla\phi^{X(T)}=(1/e)\nabla\mu^{X(T)}+(1/e)S_X^*\nabla T. \quad \text{(X-11)}$$

The change in electrical potential in a distance Δx is then

$$\Delta\phi^{X(T)}=\frac{1}{e}\Delta\mu^{X(T)}+\frac{1}{e}S_X^*\Delta T$$
$$=\frac{1}{e}\left(\frac{\partial\mu^{X(T)}}{\partial T}+S_X^*\right)\Delta T. \quad \text{(X-12)}$$

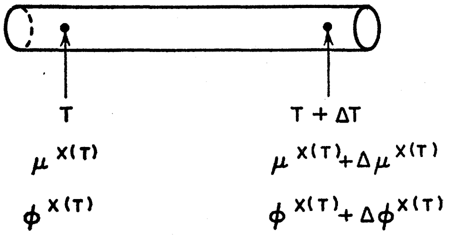

FIG. 19. Cylindrical rod of a single homogeneous chemical phase with temperature gradient but no electrical current; the temperature gradient gives rise to a gradient of the electrochemical potential, which in turn is separable into gradients of chemical and electrical potentials.

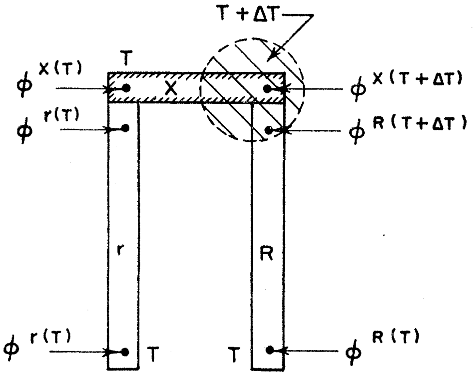

FIG. 20. The "homogeneous thermoelectric potential difference" $\phi^{X(T+\Delta T)}-\phi^{X(T)}$ cannot easily be deduced from the potentiometrically measured electrical potential difference $\phi^{r(T)}-\phi^{R(T)}$.

Thus in Fig. 19 the change $\Delta\phi^{X(T)}$ in electrical potential in going from the region at temperature T to the region at $T+\Delta T$ in the phase X is given in part by the thermostatic quantity $\partial\mu^{X(T)}/\partial T$ and in part by the transport quantity S_X^*. This electrical potential difference $\Delta\phi^{X(T)}$ has been called[2] a "homogeneous thermoelectric potential difference," referring to the fact that the potential gradient exists within a homogeneous phase as a result of a temperature gradient, whereas the usual thermoelectric potential difference (defined in Sec. C) involves nonisothermal junctions of two different phases. It is possible in principle to calculate this internal or homogeneous electrical potential difference if one can know both the thermostatic property $\partial\mu^{X(T)}/\partial T$ and the transport quantity S^*. It is of course no easy matter to calculate or otherwise determine these two properties, although we showed in Sec. C that S^* is essentially the absolute thermoelectric power of the phase, which is easily measurable. On the other hand, if we attempt to determine $\Delta\phi^{X(T)}$ by experiment, we are again faced with difficulties. Thus, suppose that in Fig. 20 the phase X is the one shown partially hatched, with the left end at T and the right end at $T+\Delta T$, ΔT being very small. We attempt to measure $\Delta\phi^{X(T)}\equiv\phi^{X(T+\Delta T)}-\phi^{X(T)}$ by connecting two chemically identical phases (wires) r and R onto the ends of X as shown. The upper right-hand region is at temperature $T+\Delta T$; all the rest of the system is at T. We use two different letters r and R though the two phases are chemically identical in order to allow for differences in electrical potentials. We have indicated the electrical potentials at various points in accordance with the notation described in Sec. A. The electrical potential $\phi^{r(T)}$ is uniform throughout phase r at temperature T. But when we consider the situation at the upper left-hand junction between phases r and X at the same temperature T we can only say that the electronic electrochemical potentials $\bar{\mu}^{r(T)}$ and $\bar{\mu}^{X(T)}$ are identical, but of course this is in general not so for the electrical potentials. Thus we already face the difficulty of not being able to evaluate the difference $\phi^{r(T)}-\phi^{X(T)}$ unless we have previously determined the difference between the chemical potentials $\mu^{r(T)}-\mu^{X(T)}$. This difficulty is comparable with that of knowing the quantity $\partial\mu^{X(T)}/\partial T$ in Eq. (X-12). In the phase R the electrical potential ϕ^R varies from $\phi^{R(T+\Delta T)}$ at the top to $\phi^{R(T)}$ at the bottom. This difference between the electrical potential at the top and at the bottom in phase R is given by an expression identical with (X-12) except with R subscripts. The electrical potential at the $T+\Delta T$ junction between phases X and R is discontinuous, just as at the junction between r and X, so that as before we cannot know the value of $\phi^{X(T+\Delta T)}-\phi^{R(T+\Delta T)}$ without first knowing $\mu^{X(T+\Delta T)}-\mu^{R(T+\Delta T)}$. We shall see that it is easy to determine the electrical potential difference $\phi^{r(T)}-\phi^{R(T)}$ by experiment, since r and R represent identical chemical phases and since the lower ends of r and R have the same temperature T. The important point is that in view of the difficulties just mentioned we cannot easily use this measured value of $\phi^{r(T)}-\phi^{R(T)}$ to determine the internal or "homogeneous thermoelectric potential difference" $\phi^{X(T+\Delta T)}-\phi^{X(T)}$.

Example 4. Electrical Potential Gradient in a Nonisothermal, Chemically Inhomogeneous Phase Carrying an Electrical Current

We want to find an expression for the local electrical potential gradient in terms of local electrical current density, temperature, and chemical potential gradients. Using again the symbol **J** for electrical current density, with $\mathbf{J}=-e\mathbf{J}_e$, upon substitution of (19) and (X-7) into (3) we find the desired relation

$$\nabla\phi=(1/e)\nabla\mu+(1/e)S^*\nabla T-(1/\sigma)\mathbf{J}. \quad \text{(X-13)}$$

In deriving this equation we have separated the electrochemical potential gradient into an electrical and a chemical part, and we have taken the current carrier to be an electron of charge $-e$. If more generally we take the carrier to have a charge q, the equivalent expression becomes

$$\nabla\phi=-(1/q)\nabla\mu-(1/q)S^*\nabla T-(1/\sigma)\mathbf{J}, \quad \text{(X-14)}$$

with $\mathbf{J}=q\mathbf{J}_e$. We emphasize that all of our equations are restricted to systems which have throughout only a single current carrier, be it electronic, hole or ionic carrier; the equations are more complicated if there are two or more types of carriers within a single phase.

Returning to Eq. (X-13) we see that an electrical potential gradient can be set up by any or all of three factors; namely, a chemical potential gradient, a temperature gradient, or an electrical current. We have treated the special case in which $\nabla\mu=\nabla T=0$ in Example 1 (Appendix B), and the case $\mathbf{J}=0$ in Example 3. We shall refer to relations (X-13) and (X-14) as the generalized Ohm's law. The current density **J** and the temperature gradient ∇T are easily and independently controllable, whereas $\nabla\mu$ is not quite an independent variable. One can set up a certain gradient of μ by making a substance chemically inhomogeneous, but if a temperature gradient is then established in the substance there will generally be an additional component in the gradient of the chemical potential. In other words, in addition to being sensitive to a composition gradient, $\nabla\mu$ is also sensitive to the local temperature gradient.

Example 5. Electrical Potential Gradient in an Isothermal, Chemically Inhomogeneous Substance without Electrical Current

If in (X-13) we set $\nabla T=\mathbf{J}=0$ we find that there is an electrical potential gradient inside a chemically inhomogeneous substance given by

$$e\nabla\phi=\nabla\mu, \quad \text{for} \quad \mathbf{J}=\nabla T=0, \quad \text{(X-15)}$$

provided the substance can carry electrical current by electrons only. If we write $\mathbf{E}=-\nabla\phi$ and call **E** the electric field intensity inside the substance, then we can compare the present situation with that involving a very high isothermal column of a gas in a gravitational field **G**. In the latter problem we have a vertical pressure gradient brought about by the gravitational field. There is also in this case a vertical density gradient. If it were not for the gravitational field, the condition for mass-motion equilibrium of the gas would be $\nabla P=0$, P being the pressure. But with the gravitational field, ∇P cannot vanish and it is just this gradient which "annuls" the effect of the gravitational field. Similarly, in the case of Eq. (X-15) the chemical potential gradient "annuls" the effect of the electric field. The condition generally laid down for electrical equilibrium (i.e., for $\mathbf{J}=0$) in a conductor, namely $\nabla\phi=0$ or $\mathbf{E}=0$, is thus valid only in a chemically homogeneous phase having a uniform temperature throughout.

Example 6. Change in Electrochemical Potential across a Resistive Isothermal Junction Carrying an Electrical Current

Consider an isothermal junction between two different homogeneous wires X and R as shown in Fig. 21. If the total resistance of the X wire is R_X and that of the R wire is R_R, it is always found experimentally that the total resistance of the composite wire AB is greater than R_X+R_R, the additional resistance R_s generally being called the "contact resistance" of the junction between the wires. In general, this contact resistance arises from the fact that in the joining process there is always formed a sheath of some sort whose composition is different from that of either X or R. In the case of two metals X and R, for example, there will always be formed an alloy-layer or sheath, usually complicated by the formation also of oxides if the joining is done in air. For our purposes we can imagine this sheath to be a fairly well-defined region as shown in Fig. 21.

If there is no electrical current flowing through the junction and the whole system A to B is at a uniform temperature, then the electronic electrochemical potential is uniform throughout and is thus continuous as we pass from phase X to phase R through the resistive sheath. Suppose now that we pass a total current i

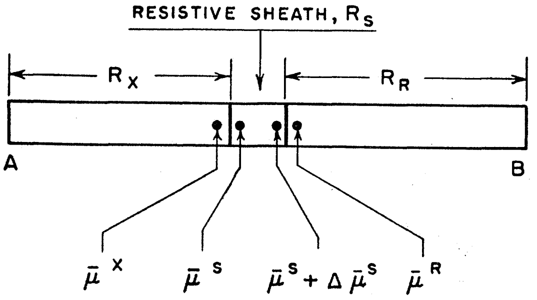

Fig. 21. The jump in electrochemical potential in crossing an isothermal junction between two wires depends upon the "contact resistance" and upon the electrical current through the junction.

through the wires and junction. Since the sheath is certainly not chemically homogeneous we cannot attribute an electrochemical potential gradient in it wholly to a gradient in the electrical potential. But from either (3) or (X-13) we can easily write

$$\nabla\bar{\mu}^s = (e/\sigma)\mathbf{J}, \tag{X-16}$$

again considering the current carriers to be electrons. If we idealize the sheath structure to be nonuniform only axially and assume that its chemical properties are uniform over any given cross section, then we have from (X-16) for the total change $\Delta\bar{\mu}^s$ in electronic electrochemical potential across the sheath,

$$\Delta\bar{\mu}^s = \int_0^d d\bar{\mu}^s = \int_0^d \frac{e}{\sigma}\frac{i}{A}dx = ei\int_0^d \frac{\rho}{A}dx = eiR_s, \tag{X-17}$$

where i is the total current, ρ is the isothermal resistivity at a given cross section, d is the thickness of the sheath of cross section area A, and R_s is the total resistance of the sheath, or contact resistance as defined above. Thus, in passing from phase X to phase R across the junction, the electrochemical potential undergoes a discontinuity eiR_s. If the two isothermal and homogeneous phases X and R happen to be chemically identical, then the discontinuity in the electrochemical potential across the junction can be easily measured, since in this case $\Delta\bar{\mu}$ between the two identical phases (at the same temperature) is just the difference $-e\Delta\phi$ in electrical potential (times $-e$) in these two phases at points very near and on opposite sides of the junction. If the phases X and R are each homogeneous but different from each other, the jump in $\bar{\mu}$ can still be measured, but in a slightly less direct way. This question is discussed in Appendix D.

A serious fault in the argument used to derive Eq. (X-17) is that the sheath or junction will often be so thin that it may be meaningless to define the space variation of electrochemical potential within the junction. If this is so, one must use indirect methods for determining the jump in potential across the junction. In some discussions[1] it is assumed that the electrochemical potential is continuous across a real junction even when current flows through the junction. Although this assumption is in general not permissible, it may be used for defining the Peltier heat and Peltier entropy at a junction, because for this latter purpose one must necessarily eliminate or in some way separate the Joule heat in the same way as is necessary in defining the Thomson heat. (This separation of the Joule heat will be mentioned again in Sec. D.)

Example 7. Isothermal Volta Potential Difference and the True Work Function

We consider next two bent rods, having the forms (with disk-shaped ends) shown in Fig. 22, of different but homogeneous isotropic chemical phases such as pure copper and pure silver. In this example we shall often refer to the phases as metals. We do this only for convenience, and the analysis holds for other phases than metallic. The rods are both at the same temperature and are located in an electric field-free evacuated space and are each originally uncharged. We discuss first the situation *before* the ends P'' and Q'' are brought into electrical contact. We assume first that the surfaces are uniform from point to point. In this case the electrical (electrostatic) potential ${}_i\phi^v$ is the same throughout the vacuum space surrounding the two metals, including the points P and Q which are, respectively, just outside metal disk X and disk R. We can refer all electrochemical potentials to the same zero level as for this uniform electrical potential level ${}_i\phi^v$. We can let ${}_i\bar{\mu}^X$ and ${}_i\bar{\mu}^R$ be, respectively, the electrochemical potentials of electrons in X and R, and ${}_i\mu^X$ and ${}_i\mu^R$ be the chemical potentials in X and R. Let ${}_i\phi^X$ and ${}_i\phi^R$ be the electrical potentials inside metals X and R. Then we can write

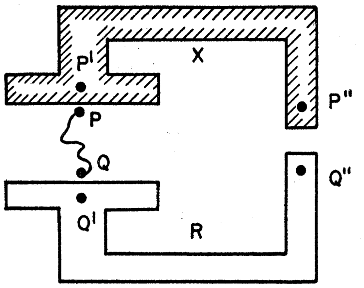

FIG. 22. Schematic arrangement for defining the isothermal Volta potential difference and the true work function; in actual measurement of Volta potential differences the ends P'' and Q'' are electrically connected.

$${}_i\bar{\mu}^X = {}_i\mu^X - e{}_i\phi^X, \tag{X-18}$$

$${}_i\bar{\mu}^R = {}_i\mu^R - e{}_i\phi^R. \tag{X-19}$$

The subscripts i refer to the initial states, i.e., before the regions P'' and Q'' are brought into contact.

The true work function eW^X of a uniform metal surface X is defined[35] as the difference between the electrical potential energy $-e{}_i\phi^v$ of an electron in the vacuum just outside the surface X and the electrochemical potential ${}_i\bar{\mu}^X$ of an electron just inside metal X. In the present case, with the temperature uniform throughout rod X and electrical potential ${}_i\phi^v$ uniform throughout the surrounding evacuated space, we do not actually need the specifications "just inside" and "just outside." Thus, the true work function of surface X is given by

$$eW^X = -e{}_i\phi^v - {}_i\bar{\mu}^X. \tag{X-20}$$

Similarly, the true work function eW^R of surface R is

$$eW^R = -e{}_i\phi^v - {}_i\bar{\mu}^R. \tag{X-21}$$

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[35] See Herring and Nichols, reference 5. These authors give a thorough discussion of the effects of surface "patches," etc.

There is no harm in letting the potential ${}_i\phi^v$ be the reference level for the electrochemical potentials, and this is equivalent to setting ${}_i\phi^v$ equal to zero. If we do this we find that $eW^X = -{}_i\bar{\mu}^X$ and $eW^R = -{}_i\bar{\mu}^R$, where now the electrochemical potentials are referred to the uniform potential of the surrounding space as zero. This gives us the physical meaning of the true work function of a uniform surface X: it is the average energy required to remove an electron from the bulk of the metal through the uniform surface X to a position of rest in the surrounding field-free space, with the provision that the temperature and pressure of the metal be maintained constant. The true work function should not be confused with the photoelectric work function.[36] The photoelectric work function refers to the removal of an electron possessing a particular energy in the metal, whereas the true work function refers to the removal of an electron possessing an energy equal to an average value for the electrons in the conduction band, maintaining fixed the temperature and pressure of the remainder of the electrons. If the space adjacent to the surface X is not field-free (which is the case when the two metals X and R are brought into contact, as in the Volta effect, see Appendix B), then the true work function refers to the average energy of removal of an electron through surface X to a rest position immediately outside this surface.

Now suppose that the two metal rods X and R are brought into electrical contact at the ends P'' and Q''. If the two metals after contact are maintained at the same temperature as before, the composite system consisting now of both metals comes to equilibrium with the electrochemical potential continuous across the junction and uniform throughout both metals as well as across the boundaries of the metals and into the "vacuum" surrounding the system. The evacuated space around the metals must be considered as having a very small but finite concentration of electrons; this "electron gas" is usually considered as being rare enough to satisfy the Boltzmann statistics. But we must be careful to use the same reference level for all potentials, and in this case we cannot use the level existing in the immediate vicinity of the disks. In fact we shall see that there is an electric field not only between the disks but also throughout the region surrounding the two-metal system. This field becomes negligible in regions far removed from the system, so that we may use the potential level in such a distant and field-free region as a reference for our electrochemical and electrical potentials. Therefore, let $\bar{\mu}^X$ and $\bar{\mu}^R$ be the electrochemical potentials of electrons in metals X and R, μ^X and μ^R be the chemical potentials and ϕ^X and ϕ^R be the electrical potentials inside the metals. Finally, let ϕ^{vX} and ϕ^{vR} be the electrical potentials at point P just outside surface X and at point Q just outside surface R, respectively. All these potentials are referred to the level at a field-free region far from the system. We can then write

$$\bar{\mu}^X = \mu^X - e\phi^X, \tag{X-22}$$

$$\bar{\mu}^R = \mu^R - e\phi^R, \tag{X-23}$$

$$\bar{\mu}^X = \bar{\mu}^R. \tag{X-24}$$

These potentials are all in general different from the corresponding ones in Eqs. (X-18) and (X-19), and in fact would all, except for the chemical potentials, be different even if they referred to the same zero level. The reason for this is that when we connect the two metals electrically, electrons flow from one metal to the other for a very short time until the electrochemical potential is the same on both sides of the boundary at the junction $P''Q''$. This new charge distribution gives rise to an electric field in the neighborhood of the compound system, as we can see from the following considerations. Imagine that we very slowly carry an electron from point Q to point P, then into the metal to point P', to point P'' still in metal X, across the boundary to Q'', then to Q' and finally to the original point Q. The path from Q to P can be any path whatever so long as we remain in the vacuum, since the electric field is a conservative one. All transfers involved are done under conditions of constant temperature and pressure of the compound system. The changes in electrochemical potential of the electron at each step are given as follows:

$$Q \text{ to } P: \quad -e\phi^{vX} - (-e\phi^{vR}), \tag{X-25}$$

$$P \text{ to } P': \quad \bar{\mu}^X - (-e\phi^{vX}), \tag{X-26}$$

$$P' \text{ to } P'': \quad \bar{\mu}^X - \bar{\mu}^X = 0, \quad \text{for uniform temperature,} \tag{X-27}$$

$$P'' \text{ to } Q'': \quad \bar{\mu}^R - \bar{\mu}^X = 0, \quad \text{at equilibrium,} \tag{X-28}$$

$$Q'' \text{ to } Q': \quad \bar{\mu}^R - \bar{\mu}^R = 0, \quad \text{for uniform temperature,} \tag{X-29}$$

$$Q' \text{ to } Q: \quad -e\phi^{vR} - \bar{\mu}^R. \tag{X-30}$$

Since the system after a complete excursion $QPP'\ldots Q'Q$ is in the same thermostatic state as it was before the excursion, no chemical changes having taken place and the temperature and pressure remaining fixed, the total change in electrochemical potential of the electron must be zero. The sum of all the changes, (X-25) through (X-30) added together, is in fact seen to vanish. The change in electrical potential between points Q and P is expressible in the customary way as a line integral of an electric vector between points Q and P. We have not specified the distance between the X and R disks, except that it would be difficult to discuss electrical potentials in the evacuated space between the opposing disk-surfaces if the separation between the latter were not large compared with interatomic distances in the two metals. Otherwise the

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[36] J. A. Chalmers, Phil. Mag. **33**, 416 (1942). See p. 428.

geometry of the system has no effect on the electrostatic potential difference given by (X-25) between points Q and P. It is obvious from elementary electrostatic theory that the electric field pattern between the disks will depend very much on the geometry of the system.

The electrical potential difference

$$V_{RX} \equiv \phi^{vX} - \phi^{vR}, \tag{X-31}$$

is called the Volta potential difference between uniform surfaces X and R, the order of the subscripts in V_{RX} indicating that the Volta potential difference is chosen as positive if the electrical potential increases as we go from a point just outside R to a point just outside X. Using the definition of the true work function given by Eqs. (X-20) and (X-21) and keeping in mind the fact that the reference level for all the potentials in (X-22) and (X-23) as well as in (X-25) through (X-30) must be the same, we can write

$$eW^X \equiv -e\phi^{vX} - \bar{\mu}^X, \tag{X-32}$$

$$eW^R \equiv -e\phi^{vR} - \bar{\mu}^R. \tag{X-33}$$

From the reasoning involved in Eq. (X-28), namely that in thermostatic equilibrium the electrochemical potential for electrons is uniform throughout our two-metal system, we now have $\bar{\mu}^X = \bar{\mu}^R$. Therefore, adding (X-28) through (X-30) and using the definitions (X-31), (X-32), and (X-33), we get after rearrangement

$$\begin{aligned} eV_{RX} &= e\phi^{vX} - e\phi^{vR} + (\bar{\mu}^X - \bar{\mu}^R) \\ &= (-e\phi^{vR} - \bar{\mu}^R) - (-e\phi^{vX} - \bar{\mu}^X) = eW^R - eW^X, \end{aligned}$$

or finally

$$V_{RX} = \phi^{vX} - \phi^{vR} = W^R - W^X. \tag{X-34}$$

The Volta potential difference V_{RX} between two uniform metal surfaces R and X is equal to the difference between the true work functions of these surfaces.

It is interesting to notice that the situation within the rare electron gas between the plates in Fig. 22, when the ends P'' and Q'' are connected, is exactly the same as that inside an isothermal, chemically inhomogeneous substance without electrical current, as discussed in Example 5 above. There it is seen that the chemical potential gradient "annuls" the electric field so that no electrical current flows. Here also, in the space between plates (Fig. 22 with P'' and Q'' connected), the electronic electrochemical potential gradient vanishes, $\nabla\bar{\mu} = \nabla\mu - e\nabla\phi = 0$, but the gradients of chemical and electrical potential do not vanish. The gradient $\nabla\phi$ is in fact just the Volta potential gradient.

As pointed out by Herring and Nichols,[5] the relation (X-34) is exact if the temperature is uniform throughout the system, and it is incorrect to add a term equal to the Peltier heat at the X-R junction. In this connection, we make two comments. First, the incorrect addition of this Peltier heat term stems from an insistence on locating a rather nebulous "electrical contact potential difference" at some special boundary or contact in the system, according to one or another of the so-called "contact theories" or "chemical theories" of contact potentials. This situation has been cleverly elaborated and clarified by J. A. Chalmers[36] in a series of papers in 1942; it is too bad that these papers have not been more widely read. Chalmers introduces quantities which he calls internal and external potential differences, and with these he shows how the "contact theories" can be brought into harmony with the "chemical theories." It seems that it should be possible to avoid the use of Chalmers' terminology and yet resolve the difficulties, inconsistencies, and opposing arguments in the same clear fashion as has been done by Chalmers. It should be possible to do this without introducing any other potentials than the electrochemical potential together with its separation into a chemical and an electrical part. We have attempted to do so at least within the limits of the subject matter to which the present Review is restricted. Chalmers' treatment of the relation between the Volta potential difference and the Peltier heat is incorrect, in our opinion, and this brings us to our second comment in connection with the addition of a Peltier heat term to expression (X-34). The Volta potential difference is essentially a thermostatic quantity whereas the Peltier heat is a true thermodynamic or transport quantity. Now we have tried to emphasize the basic difference between thermostatic and transport quantities; in fact, we stress the basic independence of these quantities. We would consider it quite possible and conceivable that two metals, say, might have identical thermostatic properties, at least over a narrow temperature range, and yet have radically different transport properties. This possibility precludes the existence of relations between essentially thermostatic parameters and essentially transport parameters.

Example 8. Nonisothermal Volta Potential Differences

Consider now a system like that in Fig. 22, except that the ends P'' and Q'' of the metal rods X and R have been electrically connected and are at a temperature $T+\Delta T$ slightly higher than that of the left-hand portion of the system. The disks at the left-hand ends are still at the same uniform temperature T. We show the new arrangement in Fig. 23, where the electrochemical potentials are indicated at various locations in the phases X and R. The electrochemical potentials at points P and Q (in "vacuum") are equal to each other and equal to that inside the metals at P' and Q'; i.e., $\bar{\mu}$ is uniform throughout the left-hand region at temperature T. The Volta potential difference $V_{RX}^{\Delta T \neq 0}$ between uniform surfaces X and R at temperature T is defined by the relation

$$eV_{RX}^{\Delta T \neq 0} = e\phi^{vX(T)} - e\phi^{vR(T)}, \tag{X-35}$$

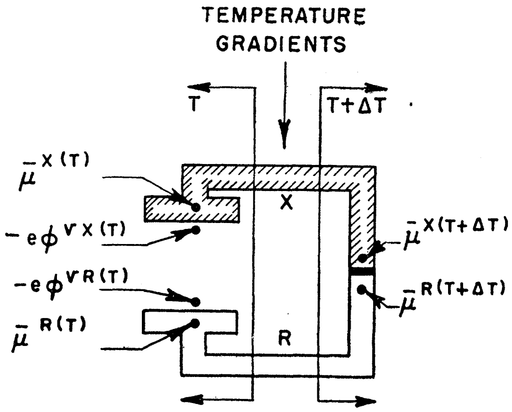

FIG. 23. One arrangement for measuring a nonisothermal Volta potential difference. The arrangement usually used in the laboratory is shown in Fig. 26.

where the superscripts $vX(T)$ and $vR(T)$ indicate that the potentials are the values in the vacuum just outside surfaces X and R which are at temperature T. The superscript notation $\Delta T\neq 0$ on the Volta potential difference will be used to indicate that the system is not isothermal throughout. Thus the "isothermal Volta potential difference" will be denoted by $V_{RX}{}^{\Delta T=0}$. The true work functions $W^{X(T)}$ and $W^{R(T)}$ of uniform metal surfaces X and R at temperature T are defined by

$$eW^{X(T)}=-e\phi^{vX(T)}-\bar{\mu}^{X(T)}, \qquad \text{(X-36)}$$

$$eW^{R(T)}=-e\phi^{vR(T)}-\bar{\mu}^{R(T)}. \qquad \text{(X-37)}$$

Substituting (X-36) and (X-37) into (X-35) one obtains

$$eV_{RX}{}^{\Delta T\neq 0}=eW^{R(T)}-eW^{X(T)}+\bar{\mu}^{R(T)}-\bar{\mu}^{X(T)}. \qquad \text{(X-38)}$$

We see that this nonisothermal Volta potential difference differs from the isothermal value given by (X-34) in that the last two terms in (X-38) cancel in the isothermal case whereas they do not in the nonisothermal case. Our problem then is to evaluate the difference between the electrochemical potentials in (X-38). From Eq. (X-10) we can find the electrochemical potential in the $T+\Delta T$ region in terms of its value in the T region, taking the spatial separation of the two regions to be Δx; this is legitimate if ΔT is small:

$$\bar{\mu}^{X(T+\Delta T)}=\bar{\mu}^{X(T)}+\nabla\bar{\mu}^{X(T)}\Delta x=\bar{\mu}^{X(T)}-S_X{}^*\nabla T\cdot\Delta x,$$

or

$$\bar{\mu}^{X(T+\Delta T)}=\bar{\mu}^{X(T)}-S_X{}^*\Delta T. \qquad \text{(X-39)}$$

The junction at the right-hand side of Fig. 23 is isothermal and has no current flowing through it; therefore the electrochemical potentials of an electron in phases X and R in this region at $T+\Delta T$ are equal. Hence when we substitute the electrochemical potentials at T from Eq. (X-39) and the corresponding expression for the R phase into (X-38), the difference $\bar{\mu}^{R(T+\Delta T)}-\bar{\mu}^{X(T+\Delta T)}$ vanishes and we come out with

$$eV_{RX}{}^{\Delta T\neq 0}=eW^{R(T)}-eW^{X(T)}+(S_R{}^*-S_X{}^*)\Delta T. \qquad \text{(X-40)}$$

When $\Delta T=0$, (X-40) reduces to the isothermal case (X-34). We shall see in Sec. C that the difference $S_R{}^*-S_X{}^*$ at temperature T is related to the relative thermoelectric power S_{XR} of a thermocouple formed by the phases X and R in the manner

$$S_R{}^*-S_X{}^*=eS_{XR}. \qquad \text{(X-41)}$$

Equation (X-40) becomes

$$V_{RX}{}^{\Delta T\neq 0}=V_{RX}{}^{\Delta T=0}+S_{XR}\Delta T. \qquad \text{(X-42)}$$

Thus if in Fig. 23 the electrostatic potential difference between points P and Q is measured with the entire system at uniform temperature T, one finds $V_{RX}{}^{\Delta T=0}$, the ordinary isothermal Volta potential difference. If the junction temperature is raised a small amount ΔT while the disks are kept at temperature T, one finds the additional[37] potential difference $S_{XR}\Delta T$. We can say that the incremental increase in the nonisothermal Volta potential difference (X-42) is just the relative thermoelectric power of phase X relative to phase R, multiplied by ΔT, and as ΔT becomes infinitesimally small,

$$\frac{dV_{RX}{}^{\Delta T\neq 0}}{dT}=S_{XR}=\frac{1}{e}(S_R{}^*-S_X{}^*). \qquad \text{(X-43)}$$

For finite ΔT we can write the integral form of (X-43) as follows:

$$V_{RX}{}^{T\neq T_0}=V_{RX}{}^{T=T_0}+\int_{T_0}^{T}S_{XR}dT$$

$$=V_{RX}{}^{T=T_0}+\frac{1}{e}\int_{T_0}^{T}(S_R{}^*-S_X{}^*)dT, \qquad \text{(X-44)}$$

where now T_0 is the temperature at the left-hand region of Fig. 23 and T is that at the right-hand region. We emphasize two points in connection with (X-43). First, the derivative refers to the temperature variation of the Volta potential difference in a nonisothermal system; and second, the thermoelectric power S_{XR} is a strictly thermodynamic or transport parameter. We shall presently discuss an equation (Eq. (X-45)) relating the temperature derivative of the isothermal Volta potential difference to the derivative of the difference between the true work functions for the two metal surfaces X and R. The equation follows simply from relation (X-34) and is in form quite similar to (X-43), with the fundamental difference that the formula to be discussed pertains throughout to a thermostatic situation whereas (X-43) pertains, as we have already emphasized, to an essentially thermodynamic or transport problem. Before

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[37] For most combinations of metals X and R and a ΔT of several degrees the second term on the right-hand side of (X-42) is practically negligible compared with the first term.

discussing this thermostatic formula we should mention that the temperature distribution indicated in Fig. 23 is not the one ordinarily used in such nonisothermal measurements. The usual arrangement[38] involves keeping at a uniform temperature all the lower and right-hand portions (including all junctions) of a system like that in Fig. 23, and varying the temperature of the upper plate. The analysis of such a system will be given presently.

We have emphasized the fact that the Volta potential difference is highly characteristic of the surfaces of metals X and R. The extreme importance of the nature and "cleanliness" of the metal surfaces in the measurement of the Volta potential difference has been very clearly demonstrated not only by the widespread disagreement of the numerical values reported in the literature for the same (bulk) metals, but also by the direct experimental demonstration[39,40] that the Volta potential difference depends upon the crystallographic planes of the metallic surfaces, even in the case of cubic crystals.

In Figs. 24(a) and (b) we have shown schematically the way in which the electric field lines-of-force may be distributed in the immediate vicinity of a metal surface. This surface is pictured as being made up of "patches," indicated by irregularly-shaped hatched areas in the figures, whose shape, size, and crystallographic orientation are determined in a very complicated way both by the physical treatment and by the chemical nature of the surface. Figure 24(a) indicates the way in which the patch fields might look[5] at the surface of a single, otherwise homogeneous chemical phase X when this phase is uncharged and is located in a field-free region; if there are other phases in the neighborhood (as in Fig. 22), they are all to be uncharged and not yet in electrical contact. The various potentials mentioned in connection with Fig. 22 and written in Eqs. (X-18) through (X-21) refer to appropriate points inside the metal bulk X and to the point P, not to points very near[41] the surface such as points a and b, because we have treated the surfaces as uniform. The reference level for these potentials is an arbitrary one at some external spot, say outside the region immediately surrounding phase X in Fig. 24(a). It is clear that there is in general a potential difference between points P and a, or P and b. If the uniform temperature of phase X is now raised, we can imagine that the geometrical arrangement of the patches becomes slightly distorted so that the field pattern changes somewhat.

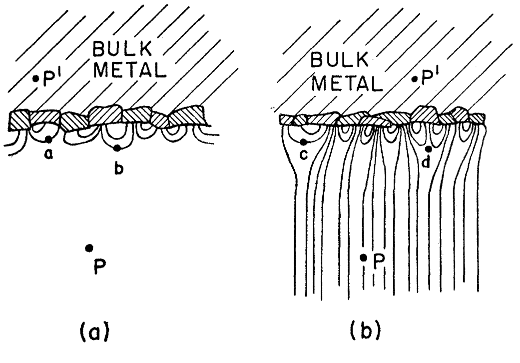

Fig. 24. Electric lines of force very near the opposing surfaces of the metal disks in Fig. 22 in vacuum: (a) before electrical contact at points P'' and Q''; (b) after electrical contact at points P'' and Q''.

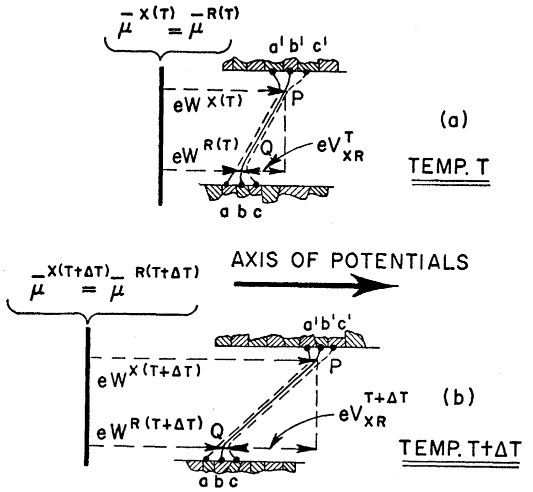

Fig. 25. Lines of electrical potential and levels of electrochemical potentials between opposing surfaces of metal disks in Fig. 22 in vacuum: (a) entire system at temperature T; (b) entire system at temperature $T+\Delta T$.

Suppose next that we have two phases X and R, as in Fig. 22, both of which are chemically homogeneous inside but which contain patches on their surfaces. We connect the ends P'' and Q'' (Fig. 22) and maintain the temperature uniform throughout. In Fig. 25(a) we show the potentials at various points in this electrically connected two-phase system. The axis of potentials is horizontal as indicated by the long heavy arrow. Because of patch effects the electric field between the plates X and R, after connection is made, becomes like that shown in Fig. 24(b) rather than like that in Fig. 24(a) which applies before connection is made. Therefore in Fig. 25(a), in passing from a point very near a given patch in surface R, on to Q and to P and to a point near an individual patch in surface X, the electrical potential varies in a manner depending upon which two end-patches we choose. But if we measure the electrical potential difference between a point Q which is ten or twenty "patch lengths" from surface R and a point P which is ten or twenty "patch lengths" from surface X, we find that this difference is independent of the regions where we begin and end. In Fig. 25(a), suppose we extend the straight line QP in both directions until it intersects the X and R surfaces.

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[38] J. G. Potter, Phys. Rev. 58, 623 (1940).

[39] H. E. Farnsworth and R. P. Winch, Phys. Rev. 58, 812 (1940).

[40] P. A. Anderson, Phys. Rev. 59, 1034 (1941).

[41] "Near the surface" means "near compared with the dimensions of an average patch."

Next we measure the electrical potentials indicated by these points of intersection, relative to the heavy vertical line at the left of the diagram. The difference between these potentials is $-eV_{RX}{}^T$, where $-e$ is the electron charge and $V_{RX}{}^T$ is the measured Volta potential difference between surfaces X and R at temperature T. It can be shown that the Kelvin method for measuring Volta potential differences, for instance, actually measures $V_{RX}{}^T$.

If the uniform temperature of the system is raised to $T+\Delta T$ the initial electrochemical potential $\bar{\mu}^{X(T)}=\bar{\mu}^{R(T)}$ within the two phases X and R changes to a new value $\bar{\mu}^{X(T+\Delta T)}=\bar{\mu}^{R(T+\Delta T)}$, as indicated by the leftward shift of the heavy vertical line in going from Fig. 25(a) to (b). From the arguments leading up to Eq. (X-34) we see that, while with P'' and Q'' connected in Fig. 22 the equality and uniformity of the electrochemical potential in both phases gives rise to the Volta potential difference V_{RX}, the actual equilibrium value of this potential does not enter into the expression for V_{RX}. But this does not mean that the Volta potential difference between two phases is independent of the bulk or volume properties of each phase. The Volta potential difference (X-34) is equal to the difference between the true work functions of the phases X and R, and the true work function for a given phase depends in general as well on the bulk properties of the phase as on its surface properties. The true work function for a given surface and phase is independent of how this phase is electrically connected (or not connected) to other phases. If one can independently and separately determine W^X and W^R for two phases (at some particular surface of each), then the Volta potential difference which will obtain when V_{RX} is measured between points just outside these particular surfaces can be calculated from (X-34).

If we differentiate (X-34) with respect to temperature,

$$\frac{dV_{RX}}{dT}=\frac{dW^R}{dT}-\frac{dW^X}{dT}, \tag{X-45}$$

we see that the temperature derivative of V_{RX} is determined completely by the way in which the true work functions of X and R vary with T. This is the thermostatic formula which we referred to above as being similar in form to (X-43); i.e., both give a temperature derivative of a Volta potential difference simply as the difference between two quantities. As already mentioned, however, in (X-43) the quantities $S_R{}^*$ and $S_X{}^*$ are transport parameters whereas in (X-45) dW^R/dT and dW^X/dT are essentially thermostatic quantities.

We now define the so-called "contact potential" at an isothermal junction between two phases X and R. At such a junction, at temperature T, we have continuity of the electrochemical potential when no electrical current is flowing; therefore by separating this potential into chemical and electrical parts we have

$$U_{RX}\equiv\phi^X-\phi^R=(1/e)(\mu^X-\mu^R). \tag{X-46}$$

We define this difference between electrical potentials in phases X and R as the contact potential difference U_{RX} at the junction between X and R, and (X-46) shows it to be equal to the difference between the electronic chemical potentials in the two phases. Comparison of (X-46) with (X-34) shows that U_{RX} and V_{RX} are not at all identical. Thus whereas V_{RX} can be measured directly, any attempt to measure U_{RX} will involve the kind of difficulties discussed above in Example 3.

Finally, if in a measurement of the isothermal Volta potential difference as in Fig. 22 one inserts any number of metals electrically connected between points P'' and Q'', an extension of the arguments involved in Eqs. (X-25) through (X-34) shows that the intermediate metals between X and R leave (X-34) unaltered. This fact is known as the Volta law of intermediate metals. It can be shown that if the metals are each chemically homogeneous, their presence in the circuit does not affect the Volta potential difference V_{RX} at temperature T even if there are temperature gradients in these intermediate phases, provided that all junctions are held at temperature T and provided that electrons are the only current carriers.

We mentioned above that the nonisothermal system for the Volta potential difference which was analyzed there is not the experimental arrangement actually used in such work. Therefore we want next to analyze the system shown in Fig. 26. Here the circuit consists of two phases X and R, the temperature T of which is uniform throughout except at the upper left-hand region where it is $T+\Delta T$ with ΔT small.

Referring to Fig. 26 we can write, for the nonisothermal Volta potential difference and for the true work functions, the expressions

$$eV_{RX}{}^{\Delta T\neq 0}=-e\phi^{vR(T)}+e\phi^{vX(T+\Delta T)}, \tag{X-47}$$

$$eW^{X(T+\Delta T)}=-e\phi^{vX(T+\Delta T)}-\bar{\mu}^{X(T+\Delta T)}, \tag{X-48}$$

$$eW^{R(T)}=-e\phi^{vR(T)}-\bar{\mu}^{R(T)}. \tag{X-49}$$

The work function and the electrochemical potential at temperature $T+\Delta T$ in (X-48) and (X-49) can be expanded in terms of the values at temperature T, and using (X-10) we find

$$eW^{X(T+\Delta T)}=eW^{X(T)}+e(dW^{X(T)}/dT)\Delta T, \tag{X-50}$$

$$\begin{aligned}\bar{\mu}^{X(T+\Delta T)}&=\bar{\mu}^{X(T)}+(d\bar{\mu}^{X(T)}/dT)\Delta T\\&=\bar{\mu}^{X(T)}-S_X{}^*\Delta T.\end{aligned} \tag{X-51}$$

Now since the electronic electrochemical potential is continuous across the X-R junction at temperature T, if we substitute (X-48) and (X-49) into (X-47), then put (X-50) and (X-51) into the resulting equation we come out with

$$eV_{RX}{}^{\Delta T\neq 0}=eW^{R(T)}-eW^{X(T)}+[S_X{}^*-e(dW^{X(T)}/dT)]\Delta T, \quad \text{(X-52)}$$

and since $W^{R(T)}$ and $W^{X(T)}$ refer to the same temperature, we may use (X-34) to get the relation

$$eV_{RX}{}^{\Delta T\neq 0}=eV_{RX}{}^{\Delta T=0}+[S_X{}^*-e(dW^{X(T)}/dT)]\Delta T. \quad \text{(X-53)}$$

If now the whole system is isothermal and we measure the Volta potential difference as the upper (X) face is gradually heated to higher temperature, the rate at which the nonisothermal Volta potential difference so measured changes, is given by

$$e(dV_{RX}{}^{\Delta T\neq 0}/dT)=S_X{}^*-e(dW^{X(T)}/dT). \quad \text{(X-54)}$$

The integral form of this relation for finite ΔT is

$$eV_{RX}{}^{T\neq T_0}=eV_{RX}{}^{T=T_0}+\int_{T_0}^{T}\left[S_X{}^*-e\frac{dW^{X(T)}}{dT}\right]dT, \quad \text{(X-55)}$$

in which T_0 is the uniform temperature of the whole system except in the upper left-hand region where the temperature is T. Relations (X-52) and (X-54) are to be compared with (X-40) and (X-43). It is interesting to notice in (X-54) that the properties of phase R do not enter at all. Thus while the actual value (X-53) of the nonisothermal Volta potential difference does of course depend on phase R, the temperature variation (X-54) does not. On the other hand, the temperature variation of the nonisothermal Volta potential difference given by Eq. (X-43), referring to the arrangement in Fig. 23, involves the thermoelectric properties of both X and R.

Herring[42] has derived an expression (his Eq. (29), p. 895) which can easily be shown to be identical with our (X-55). His equation, with our symbols, is

$$eV_{RX}{}^{T\neq T_0}=eW^{R(T_0)}-eW^{X(T)}-\int_{T_0}^{T}\int_{0}^{T}\frac{\tau_X}{T'}dT'dT.$$

Using the relation

$$W^{X(T)}=W^{X(T_0)}+\int_{T_0}^{T}(dW^{X(T)}/dT)dT,$$

we get part of Eq. (X-55), and using the relation[43]

$$\int_0^T(\tau_X/T')dT'=S_X{}^{\text{abs}}=-(1/e)S_X{}^*,$$

we get the rest of our Eq. (X-55), thus showing that our formula is identical with that of Herring.

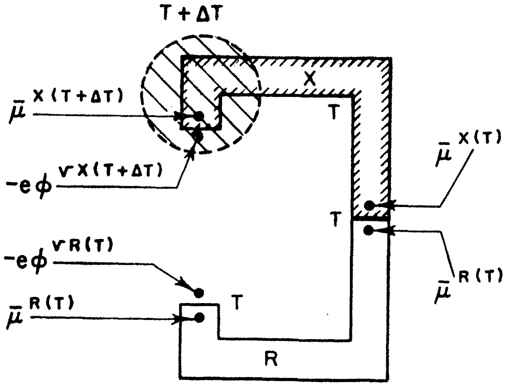

FIG. 26. Usual laboratory arrangement for measuring nonisothermal Volta potential differences.

Potter[38] has found that the temperature derivative of the true work function for polycrystalline tungsten between 300° and 900°C is independent of the state of contamination of the surface. If this is the case for other materials too, Eq. (X-54) together with Eq. (X-45) would possibly furnish a method for the measurement of absolute thermoelectric power $S_X{}^{\text{abs}}$. This latter quantity is related to the parameter $S_X{}^*$ by the expression $S_X{}^*=-eS_X{}^{\text{abs}}$. The usual methods involve either an integration of the Thomson coefficient (reduced by the absolute temperature) or else a comparison by means of the relative thermoelectric power against a material (e.g. copper) of known absolute thermopower. Actually, this method is only of academic interest, since it would probably involve large experimental errors.

APPENDIX C. POTENTIOMETRIC METHOD FOR MEASURING POTENTIAL DIFFERENCES

The potentiometric method first introduced by Poggendorf is of such great importance in potential-difference measurements that we shall consider it in detail. The most essential part of a potentiometer is a wire AB of material R and carrying an electrical current i, shown in Fig. 27. The potentiometer is supposed to measure the electrical potential difference $\phi^{XY}-\phi^{XZ}$ between the regions Y and Z inside phase X. These regions must be connected by an electrical path which allows electrical current to flow, so that when the potential difference $\phi^{La}-\phi^{Lb}$ is not zero, current can flow through the galvanometer G.[44] The leads L between A and Y and between B and Z have the same chemical composition, but are not necessarily the same

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[42] C. Herring, Phys. Rev. **59**, 889 (1941).

[43] See Sec. E.

[44] If we consider all the wire between points B and Z in Fig. 27, including that of the galvanometer-coil, to be of the same chemical phase, then since all this wire is at the same temperature the quantities $\nabla\mu$ and ∇T in Eq. (X-13) both vanish; we are left with an electrical current density J associated with the electrical potential gradient $\nabla\phi$. Thus if there is an electrical potential difference between the galvanometer terminals at a and b in Fig. 10, an electrical current will flow whose interaction with the fixed magnetic field of the instrument causes the galvanometer mirror to deflect.

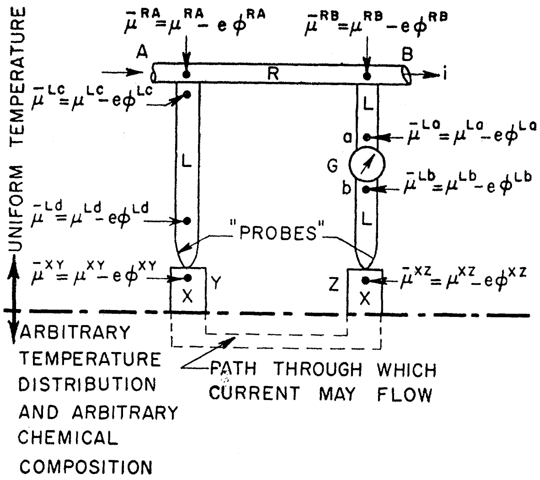

FIG. 27. The potentiometer measures the electrical potential difference between points Y and Z in the chemically identical phases X. The entire region above the heavy dotted line is at a uniform temperature.

material as in the rest of the circuit. The whole system above the heavy dotted line is held at a uniform temperature T. Below this dotted line the temperature distribution may be anything whatever. The electrochemical potentials are indicated at various important regions in the system, together with their separation into chemical and electrical terms. Since in each isothermal, homogeneous phase the chemical potential is uniform, we have

$$\bar\mu^{RA}-\bar\mu^{RB}=e\phi^{RB}-e\phi^{RA}, \qquad \text{(X-56)}$$

$$\bar\mu^{XY}-\bar\mu^{XZ}=e\phi^{XZ}-e\phi^{XY}. \qquad \text{(X-57)}$$

At balance, i.e., when there is no current flowing through the galvanometer,

$$\bar\mu^{La}=\bar\mu^{Lb} \quad \text{or} \quad \phi^{La}=\phi^{Lb}, \qquad \text{(X-58)}$$

$$\bar\mu^{Lc}=\bar\mu^{Ld} \quad \text{or} \quad \phi^{Lc}=\phi^{Ld}. \qquad \text{(X-59)}$$

Since at balance there is no current flowing through any junction and since all the junctions (above the dotted line) are isothermal, the electrochemical potential is continuous across each junction. Thus we have the four conditions

$$\bar\mu^{Lc}=\bar\mu^{RA}, \quad \bar\mu^{La}=\bar\mu^{Rb}, \quad \bar\mu^{Ld}=\bar\mu^{XY}, \quad \bar\mu^{Lb}=\bar\mu^{XZ}. \qquad \text{(X-60)}$$

From Eqs. (X-56) through (X-60) we can find the desired potential difference as follows:

$$e\phi^{XY}-e\phi^{XZ}=\bar\mu^{XZ}-\bar\mu^{XY}=\bar\mu^{Lb}-\bar\mu^{Ld}=\bar\mu^{La}-\bar\mu^{Lc}$$
$$=\bar\mu^{RB}-\bar\mu^{RA}=e\phi^{RA}-e\phi^{RB},$$

or finally

$$\phi^{XY}-\phi^{XZ}=\phi^{RA}-\phi^{RB}. \qquad \text{(X-61)}$$

If the regions Y and Z are the chemically identical terminals of a standard cell, the known electrical potential difference between these terminals (the so-called "terminal emf") in conjunction with Eq. (X-6) applied to the slidewire AB can be used to calibrate the instrument.

APPENDIX D. LABORATORY METHOD OF MEASUREMENT OF CONTACT RESISTANCE BETWEEN DISSIMILAR PHASES

We wish to analyze this method partly because of its own practical importance, and partly for the insight it gives into the question raised in Example 6 of Appendix B. There it was mentioned that if it is meaningless to assign a spatial variation of electrochemical potential within a very thin junction, then one must use indirect means for determining the jump in electrochemical potential across the junction. Figure 28 shows the setup for measuring R_s. The leads Y and X are composed of phase X and as usual we denote them by different letters to allow for differences in electrical potentials. The region inside the heavy dotted lines is isothermal while the lower ends of the leads X and Y are at room temperature. These leads are electrically connected to points P_X and P_R near the junction and are the same leads shown connected to P_X and P_R in Fig. 5 as well. Their ends P_1 and P_2 (Figs. 5 and 28) are to be connected to a potentiometer, which gives $\phi^{X(T_R)}-\phi^{Y(T_R)}$. If we know the resistivities of the phases X and R at various temperatures we can find the temperature dependence of the resistances Δr_X and Δr_R between the probe points and the junction, as indicated in Fig. 28. The electrochemical potentials for an electron at the points Q_X and Q_R very near the junction and in phases X and R, respectively, are given by Eq. (X-17), namely,

$$\left.\begin{aligned} &\text{at } Q_X\text{:} \quad \bar\mu^{X(T)}-ei\Delta r_X,\\ &\text{at } Q_R\text{:} \quad \bar\mu^{R(T)}+ei\Delta r_R,\end{aligned}\right\} \qquad \text{(X-62)}$$

the values $\bar\mu^{X(T)}$ and $\bar\mu^{R(T)}$ pertaining to points P_X and P_R. Now the potentiometer gives us $\phi^{X(T_R)}-\phi^{Y(T_R)}$, so that applying the integrated form of (X-10) as was done in (25) we can show that

$$\bar\mu^{Y(T)}-\bar\mu^{X(T)}=\bar\mu^{Y(T_R)}-\bar\mu^{X(T_R)}=-ei(\Delta r_X+\Delta r_R+R_s)$$
$$=e(\phi^{X(T_R)}-\phi^{Y(T_R)}). \qquad \text{(X-63)}$$

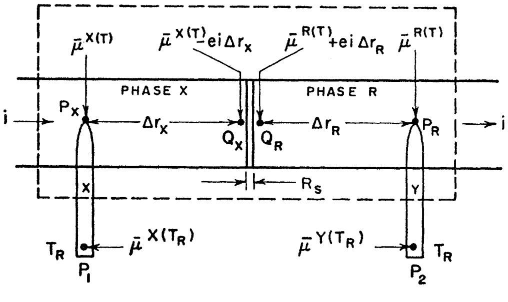

FIG. 28. Arrangement for measuring the "contact resistance" between dissimilar metal wires. The "probe leads" X and Y are of the same chemical phase and are connected to a potentiometer. The "contact resistance" R_s is obtained from Eq. (X-63).

This relation can be used in the laboratory for determining R_s, the contact resistance between dissimilar metal wires.

Returning to the question of determining the electrochemical potential jump across a junction when we cannot clearly assign a spatial variation of $\bar{\mu}$ within the junction, we can see from (X-62) and (X-63) that the jump is given experimentally by the relation

$$\Delta\bar{\mu}^s = e(\phi^{X(T_R)} - \phi^{Y(T_R)}) + ei(\Delta r_X + \Delta r_R). \quad \text{(X-64)}$$

Thus it is possible in principle by the use of potentiometrically determined electrical potential differences to find the jump in electrochemical potential across a junction through which electrical current is flowing.

APPENDIX E. RELATIONS BETWEEN THERMODYNAMIC THERMOELECTRIC PARAMETERS AND THOSE DERIVED FROM KINETIC THEORY

It was mentioned in the Introduction that under certain conditions the thermoelectric properties of some substances can be treated quite properly in terms of the ordinary thermostatic characteristics of these substances, the transport contribution in these cases being negligible or nearly so. From (64) it is seen that, except for the factor $-e$, the absolute thermopower S^{abs} of a phase is essentially the transport entropy per charge carrier S^*. And from (23), the transport entropy is related to the heat of transport per charge carrier Q^* in the manner $TS^* = Q^* - \mu$, where μ is the chemical potential per electron. Although the separation of S^* into two other terms (here Q^*/T and $-\mu/T$) can be expressed in many other ways, as can be seen from Sec. B, the particular form (23) is very useful for comparing theoretical and experimental thermoelectric powers, as follows. The usual expression for thermopower derived from kinetic theory[45] has the form

$$(\mu/eT) - (K_2/eK_1T)$$

in which K_1 and K_2 are certain transport integrals. By using series expansions for K_1 and K_2 we find another form often referred to, namely

$$\frac{\pi^2k^2T}{3e}\left[\frac{1}{\epsilon} + \frac{1}{l}\frac{\partial l}{\partial \epsilon}\right]_{\epsilon=\mu},$$

where l is the mean free path. Thus we associate the heat of transport Q^* in Eq. (23) with the kinetic quantity K_2/K_1. Now good agreement between theory and experiment has been found[46–51] in many cases of semiconductors, for which only the static contribution μ/T is used. In metals the static approximation is practically useless and even leads to the wrong sign of the thermopower.[52] In the case of semiconductors, theoretical calculations of the transport contribution at low temperatures have been made by Herring[53] and by Frederikse.[54]

APPENDIX F. TABLE OF MKS UNITS FOR THERMOELECTRIC QUANTITIES

We give in Table II a list of MKS units which may be of practical use in connection with thermoelectricity in theory and in practice.

TABLE II. List of MKS units of practical use in connection with the theory and practice of thermoelectricity.

Quantity	MKS unit
Q_J, Q_P, Q_T, Q_B	joule·meter^{-3}·second^{-1}
q_J, q_P	joule·meter^{-2}·second^{-1}
ρ_{ij}	ohm·meter
T	degree (Kelvin)
e	coulomb·particle^{-1}
J_i	ampere·meter^{-2}
x_i	meter
S_{ij}^*	joule·degree^{-1}·particle^{-1}
S_{ij}^{abs}	volt·degree^{-1}
Π_{ij}	volt
τ_{ij}	volt·degree^{-1}

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