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ILLUSTRATIONS OF THE DUAL THEORY OF METALLIC CONDUCTION

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ABSTRACT

The occurrence of a Peltier effect with change of direction within a metal crystal, which effect Bridgman has recently noted and which he has considered incapable of explanation by any of "our ordinary pictures of electrical conduction," is readily explained by the dual theory, through a formula published several years ago. Millikan's recent announcement that, according to experiments and reasoning of his own, most of the conductive electrons within metals do not share the energy of thermal agitation, while the "thermions," "presumably responsible for the Peltier and thermo-electric effects," do share this energy, tends to confirm views which the author has long held and repeatedly expressed. These facts seem to indicate that the time is opportune for a more continuous and better illustrated statement of the dual theory of metallic conduction than has yet been given. This statement reviews briefly what the theory has had to say concerning the Volta effect, Richardson's derivation of his formula for thermionic emission, and the thermo-electric pseudo equation $P=T\ dV/dT$, applying everywhere the mass law of equilibrium between electrons, ions and atoms within a metal. It then undertakes to show how the Thomson effect, the Peltier effect, the electric conductivity and the thermal conductivity of a given metal may be rationally connected by means of a set of six equations containing six constants characteristic of the metal, the equations serving for the determination of the constants. It shows in particular how a theory of heat conduction, with a definite formula for thermal conductivity, grows out of the more fundamental conceptions of the dual theory. It applies the machinery of the dual theory to the results of Bridgman's experiments on changes of electrical, thermal and thermo-electric properties of metals under high pressure, showing explicitly how the corresponding changes of the "characteristic constants" can be found and what is the nature of these changes in particular instances. Two general results of importance appear from this discussion. The first, which was predicted, is that, as a rule, compression of a metal reduces the latent heat of the ionization process within it. The conception of thermal conductivity as the product, in a general way, of electric conductivity and heat of ionization, goes far to explain why the two conductivities, though so closely related, are so differently affected by certain changes of condition. The second general conclusion from the study of Bridgman's data is that, contrary to expectation, compression of a metal increases, as a rule, the ratio of free-electron conductivity to total electric conductivity. This evidence seems to give support to the idea, already familiar, that the free electrons may go through, not necessarily between, the atoms in their progress through a metal. This conception, taken with the consideration that latent heat of ionization diminishes with fall of temperature, suggests that the supraconductive state may be one in which the distinction between "free" electrons and "associated" electrons disappears, the metal being, as regards all the conductive electrons, in a state of flux.

The theory here set forth, if it is to account for the whole of thermal conduction in metals, appears to require the heat of ionization within a metal to increase with increase of temperature, even when expansion is prevented by increase of pressure.

The dual theory indicates that photo-electric emission should be nearly independent of temperature but suggests the following revision of Richardson's thermionic emission formula, *a* being a constant:

$$i = AT^{1/2}\epsilon^{\frac{-b_0}{R}} = AT^{1/2}\epsilon^{-a}\epsilon^{\frac{aT}{T}}\epsilon^{\frac{-b_0}{T}} = A'T^{1/2}\epsilon^{\frac{-(b_0-aT)}{T}}$$

INTRODUCTION

IN THE Proceedings of the National Academy of Sciences for October, 1925, on page 611 my colleague Professor Bridgman, after stating that he has discovered a Peltier heat effect *within* metal crystals, remarks, "The mere existence of an internal Peltier heat would seem to have important bearings on our views of the nature of electrical conduction. I cannot see that any of our ordinary pictures of electrical conduction would lead us to expect a reversible absorption of heat on changing the direction of current flow." Shortly after reading this passage I asked Professor Bridgman whether he had taken account of a formula for the Peltier effect which I had published some years before.[1] He replied that he had not done so and at once admitted that the formula in question would explain the effect to which he had referred in the words I have quoted.

I shall presently give this explanation, but meanwhile I wish to say that the incident just related, showing how little the implications of the dual theory of conduction may be realized, even by one so profoundly familiar as Professor Bridgman with the phenomena and the problems of conduction, made me feel that I should now undertake to expound and illustrate the dual theory more fully, in some respects, than I have been able to do in the brief and often tentative papers which I have published on the subject during the last six or eight years, in the Proceedings of the National Academy of Sciences.

GENERAL CONCEPTION OF DUAL CONDUCTION

A paper which I published nearly twelve years ago,[2] a paper which I hope no one will now try to read *in toto*, begins thus: "Various considerations . . . . have led me to inquire whether we may not have, in the phenomena of electric conduction and of thermo-electric action in metals, the cooperation of electrons in two conditions. One condition, (A), I have conceived of as that of electrons passing from atom to atom

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[1] Hall, Proc. Nat. Acad. Sci. **7**, 62–66 (1921).

[2] Hall, Proc. Amer. Acad. Arts and Sci. July (1914).

of the metal so quickly, perhaps during actual contacts of the atoms, as not to become subject to the laws of gas pressure; the other condition, (B), I have thought of as that of electrons long enough free between the atoms to act according to the gas laws—."

I soon came to the conclusion, and for several years past all my papers on conduction, etc., have proceeded accordingly, that the (A) electrons should be regarded as having no appreciable kinetic energy dependent on the temperature of the metal, while the (B) electrons should be treated as having the thermal energy of monatomic gas molecules.

As to the relative importance of the class (A) and the class (B) electrons I have from the first held the latter, the "free" electrons, to be absolutely essential for the existence of a thermo-electric current. On the second page of the paper quoted above I say, "In all cases in which the transformation of heat into work is really understood, it is effected by means of change of dimensions, expansion and contraction of the working substance in which the heat resides and operates as molecular or atomic energy. In a thermo-electric current the electricity is the factor which undergoes a cyclic change; the metals are in a fixed state, though one of non-uniform temperature, and they neither expand nor contract after this fixed state is reached. It would seem, then, that the electricity must expand and contract in its cyclic course and serve as the vehicle and transformer of heat energy." "Thermo-electric phenomena appear to require the presence of free electrons within metals." In two later papers[3] I developed at some length the conception of mechanical action indicated in these quotations, declaring that "the part which associated electrons [electrons (A)] play in thermo-electric action is analogous to that played by entrained water in the work done by steam," not a helpful part.

On the other hand, I found evidence convincing me that these (A) electrons carry the greater part of the ordinary electric current. In my study[4] of eighteen metals, including two alloys, the largest fraction of total conductivity, at 0°C, which I assigned to the (B) electrons was 19 percent, in bismuth, the lowest being 2 percent, in iron.

All this being as stated, one can imagine with what interest and satisfaction I have read he following passage in the "abstract" of a recent paper[5] by Millikan and Eyring: "The lack of dependence of field currents drawn from metals by intense electric fields upon temperature furnishes strong evidence that most of the conduction electrons do not share in

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[3] Hall, Proc. Nat. Acad. Sci. **4,** 29–35 (1918); ibid 4, 98–103 (1918).

[4] Hall, Proc. Nat. Acad. Sci. **7,** 98–107 (1921).

[5] Millikan and Eyring, Phys. Rev. **27,** 51–67 (1926).

the energy of thermal agitation. The thermions, however, do share in this energy; they are presumably responsible for the Peltier and thermo-electric effects." Thus these authors seem to be arriving, from a starting point and by a method of their own, at a dual theory of electric conduction which resembles in important respects the one which I have been developing during the last ten or twelve years. It will be interesting to see what form their theory takes when they come to deal explicitly and in detail with thermo-electric phenomena.

FUNCTIONS OF THE POSITIVE IONS WITHIN METALS

In conduction. The idea occurred to me about eleven years ago[6] that the positive ions within a metal, being equally numerous with the "free" electrons, have probably an extremely important part to play in the conductive, or progressive, action of the "associated" electrons (A). If, ignoring the existence of these ions, we try to see how electrons can go from atom to atom, we are, or at least we should be, impressed by the lack of "terminal facilities" for such action. An electron leaving atom *a* for atom *b* must be simultaneously followed by another electron entering *a*, otherwise *a* at once becomes a positive ion; it must be simultaneously preceded by an electron leaving *b*, otherwise *b* would get an electron in excess and thus becomes a *negative* metal ion. The only way, then, to have associated-electron conduction, or progress, without the cooperation of ions is to have a lock-step electron movement extending completely around the conductive circuit. This is comparable to the action of a railway system with trains extending in unbroken continuity over every mile of the track. Something of this kind may occur in the supra-conductive state of a small homogeneous circuit, but for conductive circuits in general it is, I think, out of the question. We must, then, either put the whole burden of conduction on the "free" electrons or recognize the importance of the positive ions in furnishing "terminal facilities" for the progressive movement of associated electrons. The general, perfectly simple, conception of such progressive movement is that, when an atom comes into a certain position with respect to an adjacent ion, an electron may leave the atom, which thus becomes an ion, and join the ion, which thus becomes an atom. I should be inclined to call this conception irresistibly simple and logical if it were not for the fact that, though I have been using it freely and publicly for more than ten years, it has remained unused and apparently unrecognized by most other writers. I find that Gudden and Pohl have employed it in dealing with conduction in crystals.

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[6] See Il Nuovo Cimento, Jan.–Feb. (1915).

See Sci. Abs. no. 662 of Vol. 28 (1925) referring to a paper in the *Zeits. f. Physik*, 30, 1, pp. 14–23, 1924.

In the Volta effect. The conception just mentioned is fruitful not merely for a theory of conduction. It has an immediate bearing on the question of equilibrium at the junction of two metals. Different ions, ions of different metals, naturally have different attractive power for electrons, a fact recognized in the familiar term "ionizing potential." The ionizing potential is doubtless much less *within* a metal than in the vapor of that metal, the fact being, of course, that "free" ions within a metal are in a potential field very different from that outside the metal; but nevertheless it is altogether probable that when two different metals are joined together the ions of one metal at this junction have a greater attractive power for electrons than the ions of the other metal. So one metal, the one with the more compelling ions, gets electrons across the junction at the expense of the other metal. The result is a state of charge of the two metals, one becoming positively charged, the other negatively charged. Thus we have an extremely simple explanation of the Volta effect. This idea I have elaborated in a paper[7] published about a year ago, giving at the same time a mathematical discussion of free-electron distribution between two joined metals and between each metal and the space outside.

The simplest assumption which can be made as to the energy condition of equilibrium of "associated" electrons at the junction of two metals α and β is that the energy of an associated electron on an atom of metal α is equal to that of an associated electron on an atom of metal β, after the Volta difference of surface charge between the two metals has established itself. This condition, if admitted, explains at once the otherwise puzzling fact[8] that the amount of energy needed to expel an associated electron from metal α is the same as that required to expel an associated electron from metal β, provided in each case the expelled electron reaches the same final condition.

ACTION OF THE "MASS LAW" WITHIN METALS

In thermionic emission. I was not, I believe, the first to suggest that the mass law of equilibrium holds between the atoms, the free electrons, and the ions, within a metal, but I have made a more persistent and extensive use of this conception than anyone else has made. For example there is, in my opinion, an essential difference, highly important for soundness of theory though perhaps not easily detected by experiment,

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[7] Hall, Proc. Nat. Acad. Sci. **11,** 111–116 (1925).

[8] Millikan, Phys. Rev. **18,** 236–244 (1921).

between what occurs in an insulated piece of metal giving off thermions and a non-insulated piece of metal giving off thermions. The difference to which I here refer is not the obvous fact that the insulated metal acquires a positive charge by losing electrons. It would hold and hold to practically the same extent, if each of the pieces of metal dealt with were so large, and the number of electrons lost so small, that the effect of static charge on the insulated metal would be negligibly small. This difference is that, whereas the non-insulated metal suffers no change of condition in giving off electrons, because electrons in equal number are flowing into it all the time, the insulated metal is really losing some of its substance, the emitted electrons, and this loss entails, according to the mass law, a change within the metal, new ionization going on there to such an extent that, if n is the number of electrons lost, $n/2$ atoms suffer ionization, furnishing $n/2$ new ions and $n/2$ new free electrons. This process of ionization is accompanied by heat absorption, and the amount of this heat absorption depends on the magnitude of n, not on the size of the piece of metal.

O. W. Richardson, in the course of his thermo-dynamic argument leading to his famous expression for thermionic emission, ignored the difference just pointed out. He framed a certain equation[9] for dS, the change of entropy of his system, with reference to an insulated piece of metal, supposed to be giving off electrons, and then proceeded to apply this equation, or the consequences of it, to the case in which the metal is not insulated. I have said all this before in two papers,[10] the second of which should be read first, as the other contains a misleading, though not fundamental, error. I have little doubt that, to most of those who may have read these papers, my argument, impeaching as it does the soundness of Richardson's derivation of his familiar and practically useful expression for thermionic emission, has appeared to be unimportant if not absurd. Let me, then, call attention to the fact that, although the criticism in question is in form and in substance of my own independent making, others have detected and pointed out the fallacy of Richardson's reasoning. See, for example, a paper on *The Universal Constant of Thermionic Emission*, by Bridgman, in the PHYSICAL REVIEW for February, 1926, in which mention is made of the fact that Richardson has rather recently[11] admitted at least a formal error in the argument referred to.

The "equation" $P = T\,dV/dT$: What precedes has a direct bearing on the validity of the reasoning leading to this quasi-equation, in which

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[9] Richardson, Emission of Electricity from Hot Bodies, p. 28.

[10] Hall, Proc. Nat. Acad. Sci. **4,** 11, 13 (1918); ibid **5,** 197–198 (1919).

[11] Richardson, Proc. Roy. Soc. **105A,** 403 (1924).

P stands for the Peltier effect and V for the Volta effect between two metals. The following passage is quoted from a paper[12] which I published about three years ago:

"Bridgman[13] has given us the history of this formula. It was first published by Lorentz, in 1889, but remained comparatively unnoticed and was re-derived by Kelvin eight or ten years later. Lorentz, however, accepted the suggestion of Budde that there may be an absorption or evolution of heat at the free surface of the metals, and Kelvin, after finding that the formula, when tested by the experimental data available, 'failed by a thousand fold,' admitted the same possibility. Richardson,[14] however, by a new course of argument arrived at the formula as written, and K. T. Compton,[15] for the purpose of testing its correctness, undertook measurements of the 'temperature coefficient of contact potential,' (dV/dT), between nickel, which we will call metal A, and iron, which we will call B. According to his experiments this temperature coefficient, in the neighborhood of 40°C, is about 0.00165 volt per degree,"—that is, in his own words, "about fifty times as large as the theoretical coefficient," deduced from the equation in question. Compton did not, it is true, regard this test as conclusive, and he remarked, quite justly, that measurements in extremely high vacua can alone settle the question here at issue, but the evidence thus far is highly unfavorable to the claims of the relation stated.

Now the same fallacy which Bridgman and I have independently found in Richardson's discussion of thermionic emission enters into the argument by which he arrived at the formula under discussion, an "equation" one side of which is, according to the best evidence available, about fifty times as great as the other. However little harm, then, this fallacy may have done in the one case, it seems to have been mischievous in the second.

My own theory of the matter, set forth briefly in the paper from which the passage above given is taken, adds to the Peltier heat, P, the net amount of heat absorbed by reason of the operation of the mass law, when electrons are transferred from one of two Volta-effect plates to the other. This change, with the best data available, reduces the ratio of the two sides of the equation in question from about fifty to about four in the case of the same two metals, nickel and iron, that were used by Compton. Further measurements on the temperature coefficient of the Volta effect are greatly needed.

[12] Hall, Proc. Nat. Acad. Sci. **9**, 207–211 (1923).

[13] Bridgman, Phys. Rev., **14**, 306–347 (1919).

[14] Richardson, Emission of Electricity from Hot Bodies, pp. 41 and 42.

[15] Compton, Phys. Rev. **7**, 209–214 (1916).

FORMULA FOR THE PELTIER EFFECT

I come now to my formula for the Peltier effect, the one to which I refer in the opening paragraph of this paper. This formula, derived in a paper[1] printed several years ago, is

$$\Pi_{\alpha\beta}=\left(\frac{k_f}{k}\right)_\beta\lambda_\beta-\left(\frac{k_f}{k}\right)_\alpha\lambda_\alpha,$$

where $\Pi_{\alpha\beta}$ is the Peltier effect heat absorbed in the passage of 10 coulombs, $(1/e)$ electrons, from metal α to metal β, k_f is the free-electron conductivity, k the total conductivity, λ_α the heat required to free $(1/e)$ electrons within α, and λ_β the corresponding quantity for β. Now within a single crystal of metal α and β refer merely to different directions, and evidently in this case λ_α and λ_β are equal, whereas $(k_f/k)_\alpha$ need not be the same as $(k_f/k)_\beta$. This is substantially what I said to Professor Bridgman in the conversation already referred to, and he of course conceded my point. This should not be taken to mean that he accepts my theory of conduction *in toto* or even my expression for the Peltier effect.

QUANTITATIVE HYPOTHESES: CHARACTERISTIC "CONSTANTS"

Much of what I have said thus far in this paper is of a rather general character. I must now, in attempting to embrace in one general quantitative theory all the phenomena with which I have to deal, make use of definite quantitative hypotheses or assumptions involving temperature relations. In doing this I am well aware that these assumptions may have only a very limited validity,—that is, may hold through only a narrow range of temperature. If I try, as I do, to see whether they will, without change of constants, enable me to cover the stretch from 0°C to 100°C, I do this without expecting perfect consistency of results. I simply dó what I can with a problem of great complexity, leaving my readers, whether few or many, to evaluate the fruits of my labor and decide whether the undertaking in which am engaged is worthy of their further interest and attention.

Assumption 1: The number, n, of free electrons per cu. cm. of a metal is expressed by the equation

$$n=zT^q, \tag{1}$$

where z and q are constants and T is absolute temperature. I do not, for my present purposes, find it necessary to evaluate z, the magnitude of which, for a given value of free-electron conductivity, naturally depends on the length of mean path of the "free" electrons between or through the atoms, and concerning this distance my ideas are, perhaps, neither more nor less definite than those of other writers on the subject of conduction. To those, however, who maintain that n must be an exceedingly small fraction of the number of atoms per cu. cm. of the metal or that, because of thermodynamic restrictions, n cannot vary with temperature as I would have it vary, I have addressed a special argument.[16]

Assumption 2: This is that the ratio (k_f/k), of free-electron conductivity to total conductivity, is given by the equation

$$(k_f/k)=C+C_1t_1+C_2t^2, \tag{2}$$

where C, C_1 and C_2 are constants, and t is temperature above 0°C. This is a quite familiar and innocent kind of formula, the only question about it being through what range of temperature it will hold reasonably well without the addition of more terms in higher powers of t.

Assumption 3: The heat of ionization within a metal is, in ergs per electron,

$$\lambda'=\lambda'_c+sRT, \tag{3}$$

where λ'_c is a constant, s is a constant the value of which is never less than 2.5, and R is the gas-constant for a single molecule. At first I assumed the value of s to be 2.5, just large enough to make the term sRT express the kinetic energy and the pv energy, per electron, of the gaseous condition. Later, for the purpose of dealing the better with thermal conduction, as maintained by electric action, I gave s a special value for each metal studied, making it range from 4.35 in bismuth to 15 in iron.

I had not at the beginning any intention of seeking an explanation of thermal conduction. But presently I found myself obliged to deal with it, the history of the matter being as follows: Reflection upon the internal electrical condition of an insulated metal bar kept hot at one end and cold at the other showed me that, if my conception of free-electron conduction and associated-electron conduction held, and if, as I assume in the use of Eq. (1) above, the number of free electrons per cu. cm. is greater at the hot end of the bar, the mechanical pressure-gradient of these electrons must tend to drive some of them from the hot end to the cold end, thus giving the hot end a *plus* charge and the cold end a *minus* charge. Such a condition of charge will tend to drive associated electrons up the temperature gradient of the bar. Thus we have begun a cyclic current within the insulated bar, free electrons going from hot to cold and associated electrons from cold to hot. But such a movement involves a constant process of ionization, absorbing heat, at the hot

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[16] Hall, Proc. Nat. Acad. Sci. **11**, 36–38 (1925).

end of the bar and a corresponding constant process of reassociation, giving out heat, at the cold end, and this means conveyance of heat-energy, heat conduction or heat convection, by an electrical process, along the bar. Having thus come, quite unexpectedly, on an explanation of some measure of heat conduction, I thought it worth while to inquire whether the mechanism described was capable of accounting for the whole of this conduction, and in prosecuting this inquiry I gave to the constant s the various values, characteristic of the various metals, to which I have referred. I have, however, all along regarded this as, to some extent, a tentative operation, seeing that a part, perhaps the greater part, of thermal conduction may be attributable to some other process. When such another process, capable of accounting for any large amount of heat conduction, is clearly imagined and convincingly described, it will be in order to modify my treatment of heat conduction accordingly; but meanwhile I propose to continue my endeavor to see what will come of putting the whole burden on the cyclic electric current which I have pictured above.

I have now introduced for each metal seven characteristic constants, z, q, C, C_1, C_2, λ_c' and s, with the understanding that z need not, for the present, be evaluated definitely. To determine the values of the other six constants I shall need for each metal six equations, in which these constants will appear as the only unknown quantities. Eqs. (1), (2) and (3) are not available for this purpose, as each of them contains some other unknown.

Three of the desired equations I obtain from a study of the Thomson effect, in a way now to be described. My conception of the Thomson effect is a very complicated one, as many elements necessarily enter into it, and my mathematical expression for the Thomson effect heat, σ, is correspondingly complicated.[17] This expression is derived and given as Eq. (8) in a paper[18] published in March, 1920. It is

$$\sigma = \frac{k_f}{k} \cdot \frac{3}{2} \frac{R}{e} - \frac{k_f}{k} \cdot \frac{RT}{ne} \cdot \frac{dn}{dT} + \frac{\lambda'}{e} \cdot \frac{d(k_f/k)}{dT}, \qquad (4)$$

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[17] In this connection I wish to quote with approval the following passage from the *Conclusion* of Bridgman's paper on *Thermo-electric Quality under Pressure* (Proc. Amer. Acad. Arts and Sci. **53,** March (1918):

"The results suggest most strongly that the thermo-electric mechanism must be comparatively complicated, that it cannot be at all of the simplicity imagined by the free electron theory and that most likely the effect which we measure are the resultant of different effects, which sometimes, at least, work in opposite directions."

[18] *Inferences from the Hypothesis of Dual Electric Conduction; The Thomson Effect.* Proc. Nat. Acad. Sci. **6,** 139–154 (1920). In this paper s had the value 2.5, and accordingly some of the equations it contains were, when s was given a more general value, revised in a subsequent paper, *The Thomson Effect and Thermal Conduction in Metals,* Proc. Nat. Acad. Sci. **6,** 613–621 (1920).

where R is the gas-constant, 1.37×10^{-16}, and e the electronic charge, 1.59×10^{-20}.

Making use of Eqs. (1), (2) and (3), I reduce (4) to the form

$$\sigma = K + (K_1 + K_2 t)T \tag{5}$$

in which K, K_1, and K_2 are constants defined by the equations

$$K = \frac{R}{e}\left[C(1.5-q) + C_1\left(\frac{\lambda_c'}{R} - 273\,(1.5-q)\right) - 273C_2\left(\frac{2\lambda_c'}{R} - 273(1.5-q)\right)\right] \tag{6}$$

$$K_1 = \frac{R}{e}\left[C_1(s+1.5-q) + C_2\left(\frac{2\lambda_c'}{R} - 273\,(1.5-q)\right)\right] \qquad (7)^{19}$$

$$K_2 = \frac{R}{e} \cdot C_2(2s+1.5-q) \qquad (8)^{19}$$

The value of σ was put into the form of Eq. (5) in order to make it agree, as nearly as possible, with the expression used by Bridgman in his paper, already referred to, on *Thermo-electric Quality under Pressure.*. All or very nearly all of the thermo-electric data which I have used in the quantitative development of my theories during the past six or eight years are taken from this paper, and I do not see how I could have made progress except on the basis of Bridgman's work.

He writes, in substance, the equation

$$\sigma = (A + Bt)T, \tag{9}$$

where A and B are constants. He found from his experiments nothing corresponding to my constant K, which I nevertheless have been unable to get rid of in my general expression for σ. On the other hand, there is nothing in my reasoning to show that the value of K may not be very small. Accordingly, on the ground of experimental evidence, as expressed in Eq. (9), I put K equal to zero, thus reducing (6) to the form

$$C = \left[-C_1\left(\frac{\lambda_c'}{R} - 273\,(1.5-q)\right) + 273C_2\left(\frac{2\lambda_c'}{R} - 273\,(1.5-q)\right)\right] \Big/ (1.5-q). \tag{10}$$

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[19] These two equations had a somewhat different form in the first of the two papers mentioned in the last preceding footnote.

As to my K_1 and K_2, I take these to be, respectively, the same as the A and B of Eq. (9), and, as Bridgman gives the values of A and B for every case which I deal with, I have the K_1 and K_2 in Eqs. (7) and (8) replaced by definite numerical quantities. Thus in (7), (8) and (10) I have three of the six equations needed to determine the values of the six constants q, C, C_1, C_2, λ_c' and s, with which I have to do. Of course, the values of A and B, like all other experimentally found data that I have to use, are subject to some errors, and such errors may have appreciable consequences in the results I draw from my equations. Bridgman's values of σ were not found by direct observation but were derived by double differentiation from the directly observed electromotive forces of thermo-electric couples, and they all assume the value of σ to be zero in lead.

The fourth equation to be used in evaluating the six constants is an expression for the thermal conductivity, framed in accordance with the conceptions already set forth in this paper. This is correctly given as Eq. (12) in a paper[18] which I published in 1920, but in the derivation which that paper gives of the equation there is an assumption,[20] explicitly made, which is unnecessary and should be eliminated. In view of this fact and of the further fact that my theory of thermal conduction was, so far as I know, an entirely novel conception, I shall repeat and revise here the argument in question. I shall begin by repeating, with some change of form, a discussion given on page 100, Vol. 4, of the National Academy Proceedings.

In addition to the potential P, due to electric surface charge, we must now think of a potential, P_a, due to the attractions or repulsions of adjacent matter for the associated electrons, and also of a potential, P_f, due to the attractions or repulsions of adjacent matter for the free electrons. Both classes of electrons are subject to the charge-potential P, but associated electrons only are subject to the potential P_a, and free electrons only to the potential P_f. According to my sign convention electrons tend to move in the direction of *decreasing* potential.

According to my conception of thermal conduction, as already set forth, the condition of equilibrium, mobile equilibrium, within an insulated metal bar kept hot at one end and cold at the other is that the down-temperature free-electron stream at any cross-section of the bar shall be equal to the up-temperature associated-electron stream, which is obviously, the length l of the bar being measured from the cold end,

[20] That $(d\,P_a/d\,T)$ is negligibly small.

$$-k_a\cdot\frac{d(P+P_a)}{dl},$$

per unit area of cross-section at the same place. For simplicity let the bar have unit cross-section; let m equal the mass and e the charge of an electron; let μ equal the coefficient of mobility of the free electrons through the metal,—that is, the velocity that one dyne would maintain in driving 1 gram of free electrons along the bar. If now we assume that the mechanical tendency of the free electrons, if acting without electric forces, would produce equality of pressure, p, from the hot end to the cold end of the bar, we have, as the mathematical expression for the condition of mobile equilibrium described above,

$$\mu\left(\frac{dp}{dl}dl/nm\cdot dl\right)ne+k_f\cdot\frac{d(P+P_f)}{dl}=-k_a\cdot\frac{d(P+P_a)}{dl},$$

which reduces to

$$\mu\frac{dp}{dl}\cdot\frac{e}{m}+k_f\cdot\frac{d(P+P_f)}{dl}=-k_a\cdot\frac{d(P+P_a)}{dl},\tag{11}$$

k_f being, as before, the the free-electron conductivity while k_a is the associated-electron conductivity.

The relation of μ to k_f can be found from the observation that, if the bar were at uniform temperature with a potential gradient (dP/dl), forming part of an electric circuit, two equivalent expressions could be found for the strength of the free-electron current,

$$\mu\left(\frac{dP}{dl}\cdot\frac{ne}{nm}\right)ne,$$

and

$$k_f\cdot\frac{dP}{dl},$$

whence we get the equation

$$\mu=k_f\cdot\frac{m}{ne^2}\tag{12}$$

From (11) and (12) we get, assuming for simplicity unit temperature gradient in the bar,

$$k_f\left(\frac{1}{ne}\cdot\frac{dp}{dT}+\frac{dP}{dT}+\frac{dP_f}{dT}\right)=-k_a\left(\frac{dP}{dT}+\frac{dP_a}{dT}\right)\tag{13}$$

A little reflection shows that, as $2.5R$ represents the total mechanical energy, kinetic and potential, per electron, of the free electrons as a gas within the metal, we have, by virtue of the definitions of the several letters involved, the equation

$$P_f - P_a = \frac{1}{e}\,(\lambda_c' + (s-2.5)RT) \tag{14}$$

whence comes

$$\frac{dP_f}{dT} = \frac{dP_a}{dT} + \frac{R}{e}\,(s-2.5) \tag{15}$$

Moreover, since

$$p = nRT \tag{16}$$

and, according to Eq. (1),

$$n = zT^q$$

we have

$$\frac{1}{n}\cdot\frac{dp}{dT} = R\left(1 + \frac{T}{dT}\cdot\frac{dn}{n}\right) = R(1+q) \tag{17}$$

Substituting from (15) and (17) in (13), we get

$$k_a\cdot\frac{k_f}{k}\cdot\frac{R}{e}\,(s+q-1.5) = -\,k_a\left(\frac{dP}{dT} + \frac{dP_a}{dT}\right), \tag{18}$$

where k is the total electrical conductivity, $(k_a + k_f)$.

Now the second member of (18) is, as we have already seen, the strength of the up-temperature stream of our cyclic electric current. At the hot end of the bar the electrons of this stream become free, each absorbing in the ionizing process the amount λ', Eq. (3), of heat energy, and the amount of heat energy absorbed by the unit quantity of electricity, 10 coulombs, in passing from the associated electron state to the free-electron state is (λ'/e). Accordingly the current

$$-k_a\left(\frac{dP}{dT} + \frac{dP_a}{dT}\right)$$

will, in turning from the associated electron form to the free-electron form at the hot end of the bar, absorb

$$-k_a\left(\frac{dP}{dT} + \frac{dP_a}{dT}\right)\frac{\lambda'}{e}$$

ergs of heat energy per second. So this is the amount of heat energy which starts per second down the bar from the hot end, and, as we have assumed the bar to have unit cross-section and unit temperature gradient, this quantity is numerically equal to the thermal conductivity of the metal. Letting θ stand for this conductivity and remembering Eq. (3), we have

$$\theta = -k_a\left(\frac{dP}{dT} + \frac{dP_a}{dT}\right)\left(\lambda_c' + sRT\right)\frac{1}{e}. \tag{19}$$

Substituting from (18) for the first factor of the second member in (19), we get

$$\theta = \frac{R^2}{e^2} \cdot k_a \cdot \frac{k_f}{k}\left(\frac{\lambda_c'}{R} + sT\right)(s+q-1.5) \tag{20}$$

As θ and k are known by direct measurement, and (k_s/k) is expressed, Eq. (2), in terms of C, C_1, C_2 and the temperature, and as k_a is merely k less k_f, we have in (20) no new unknown, and this equation is therefore available in the work of evaluating our six constants q, C, C_1, C_2, λ_c' and s. In fact we have two equations of this type for our purpose, one for θ at 0°C, the other for θ at 100°C.

I will interpolate here the statement that in the eighteen metals, including two alloys, for which I have found values of these constants, the average magnitudes of λ_c' and s are such as to correspond with an ionizing potential of about one-sixth volt at 0°C within the metal. Furthermore, the average intensity of the cyclic electric current needed to account for the total thermal conductivity is, with a temperature gradient of 1 degree centigrade per cm, about 5 amperes. It must not be supposed that this current generates joulean heat. If it produces heat in some ways, it absorbs heat in other ways. It is accompanied by, and is the mechanism of, degradation of heat, conveyance of heat energy from points at high temperature to points at low temperature, but it does not, on the whole, either produce or consume heat.

We need one more equation, making six in all, for the determination of our constants. This we can get from the Peltier effect, but, as this involves two different metals, a slight complication is here encountered. If we have obtained five independent equations, of the types already shown, for each of two metals, we shall by writing for each of two temperatures, preferably 0°C and 100°C, the equation of Peltier heat between these two metals, have twelve equations in all, enough to determine the values of the six characteristic constants belonging to each metal.

In substantially this way were found those values of these constants, for each of eighteen different metals, including the two alloys constantan and manganin, which I published[4] several years ago, and which would now require some slight revision.

The process of finding such values from such equations as those given above is not altogether straightforward and precise. Owing to the shape of the equations and the fact that they are probably not wholly consistent with each other, being affected as they doubtless are by some inaccuracies of both theory and observation, it is necessary to follow a trial method in solving them, and to select as the final values of the constants those which, on the whole, come nearest to meeting the requirements expressed by the equations.

I shall presently illustrate this method of procedure by showing how I have dealt with the data found by Bridgman in his experiments on the electrical and thermal properties of certain metals under high pressure.

EFFECT OF HIGH PRESSURE ON THE "CHARACTERISTIC CONSTANTS" OF METALS

I need for my present undertaking to know the effect of pressure on electric conductivity, thermal conductivity, and thermo-electric qualities. Bridgman has, I believe, furnished all the needed data for only eight metals, bismuth, copper, iron, nickel, platinum, silver, tin, and zinc. The table given below embodies many of the results of his observations, not necessarily in the form in which he published these results.

Following the custom of my previous papers I define σ, the Thomson effect at any temperature T, as the amount of heat, in ergs, absorbed by 10 coulombs of negative electricity, $(1/e)$ electrons, in going from a place of temperature $(T-\frac{1}{2})$ to a place of temperature $(T+\frac{1}{2})$ through the metal. This makes the sign of my σ the opposite of that belonging to σ as commonly used. I define $\Pi_{\alpha\beta}$, the Peltier effect between metals α and β, as the amount of heat, in ergs, absorbed by $(1/e)$ electrons in going from metal α to metal β. This makes my sign convention for $\Pi_{\alpha\beta}$ opposite to that used by Bridgman. I call the uncompressed metal α and the compressed metal β. Bridgman has not, as a rule, made absolute determinations of electrical or thermal conductivity, but in the last two columns of the table I have undertaken to give definite values for both k_{30} and θ_{30}, the subscript indicating 30°C, the only temperature for which Bridgman gives information concerning θ. In the case of k, I have taken values of k_0 from the usual sources and have found k_{30} by applying Bridgman's coefficients. The way in which definite values of θ_{30} have been arrived at will be indicated later.

I shall presently undertake to show how and to what extent the changes of electrical and thermal qualities of metals under pressure, as exhibited in this table, can be coordinated by means of the conceptions already set forth in this paper. But first certain reservations must be noted.

It must be remembered that the machinery of my theory, in its present form, does not undertake to deal with any case in which the experimentally observed Thomson effect cannot be expressed with sufficient accuracy by means of Eq. (9). If, for example, the parenthesis of that equation contained an additional term, in t^2, I should, in order to take account of it, be obliged to complicate one or more of the simple assump-

TABLE I

	$p\left(\frac{kgm}{cm^2}\right)$	σ	$\Pi_{\alpha\beta}\times 10^{-2}$ at 0°	$\Pi_{\alpha\beta}\times 10^{-2}$ at 75°	$k_{30}\times 10^6$	θ_{30}
Bismuth	0	$-3.20T$	0	0	8.324	0.01909
	2000	$-3.20T$	-289	-369	8.056	0.01790
	4000	$(-3.20-0.021t)T$	-574	-912	7.773	0.01672
	8000	$(+1.011-0.087t)T$	-1530	-2180	7.195	0.01435
	12000	$(-1.297-0.014t)T$	-2580	-2960	6.634	0.01199
			at 0°	at 100°		
Copper	0	$-0.966T$	0	0	576	0.9110
	2000	$-0.966T$	-1.6	-2.2	578.1	0.8973
	6000	$(-0.980+0.0_436t)T$	-4.1	-7.8	582.3	0.8700
	12000	$(-0.989+0.0_432t)T$	-7.6	-15.9	588.6	0.8290
Iron	0	$(1.78+0.0516t)T$	0	0	66.57	0.1610
	2000	$(1.718+0.052t)T$	$+3.3$	-7.5	66.90	0.1609
	6000	$(1.49+0.058t)T$	$+10.9$	-14.9	67.53	0.1607
	12000	$(0.509+0.070t)T$	$+38.3$	-35.8	68.45	0.1604
Nickel	0	$3.56T$	0	0	81.98	0.1409
	4000	$3.543T$	-7.1	-15.7	82.49	0.1341
	8000	$(3.509+0.00029t)T$	-14.8	-31.5	83.00	0.1274
	12000	$(3.502+0.00032t)T$	-24.1	-49.9	83.48	0.1206
Platinum	0	$2.668T$	0	0	98.56	0.1682
	2000	$(2.628+0.0009t)T$	-7.7	-10.1	98.97	0.1677
	6000	$(2.49+0.0023t)T$	-23.0	-35.1	99.71	0.1666
	12000	$(2.32+0.0051t)T$	-44.8	-64.9	100.81	0.1650
Silver	0	$-0.864T$	0	0	597.4	1.008
	4000	$-0.875T$	-8.9	-16.1	606.0	0.9932
	8000	$-0.884T$	-16.9	-30.6	614.3	0.9784
	12000	$-0.890T$	-25.3	-44.2	622.7	0.9634
Tin	0	$1.34T$	0	0	92.92	0.1526
	2000	$(0.1351-0.0_419t)T$	0	-0.11	94.93	0.1587
	6000	$(0.1124+0.0_324t)T$	$+0.66$	-0.90	98.88	0.1668
	12000	$(0.0282+0.0012t)T$	$+4.92$	-1.75	104.6	0.1749
Zinc	0	$0.99T$	0	0	160.7	0.2645
	2000	$(0.928+0.0_434t)T$	-30.0	-63.0	162.1	0.2656
	4000	$0.891T$	-64.0	-125.0	163.6	0.2667
	6000	$0.840T$	-98.0	-190.0	165.3	0.2678
	12000	$(0.759-0.0036t)T$	-190.0	-412	169.8	0.2711

tions expressed by Eqs. (1), (2), and (3), and add another equation of the general type of (7), (8) and (10). Now, according to Bridgman's observations, the Thomson effect varies under pressure in such a way that, when it ceases to be expressible by one term, the AT of Eq. (9), it is usually not strictly expressible by two terms. It is not, therefore, surprising or discouraging to find that in some cases my apparatus proves incapable of dealing with the data set forth in this table. Moreover, the treatment of even a simple case in the method presently to be illustrated is laborious, and the treatment of any case in which σ has two terms is very tedious, though I have carried it through in several instances to be indicated later. My discussion, then, of the data presented in the table above has not been exhaustive, though it has been sufficiently extended to be generally representative.

My inquiry is this: It being assumed that known values of the six "characteristic constants," q, s, λ_c', C, C_1, C_2, correspond with sufficient accuracy (they do not correspond perfectly) to the electrical and thermal properties, at normal pressure, of the metals dealt with, what changes of these constants will correspond to the observed changes of these electrical and thermal properties under the pressures used by Bridgman?

BISMUTH

I shall deal first with bismuth. The values of the characteristic constants for this metal, as given in my *Summary*, printed in the Proceedings of the National Academy of Sciences for March, 1921, are as follows:

q	s	λ_c'	C	$C_1\times 10^6$	C_2
1.20	4.35	1088×10^{-16}	0.19	-80.4	0

I keep the first two of these as they stand; the third I put into the more convenient but substantially equivalent form $\lambda_c' = 790R$, where R is the gas constant 1.37×10^{-16}. For C and C_1 I now get, as will be seen, slightly different values, by taking e as 1.59×10^{-20}, whereas in making the tables of my *Summary* I took e as 1.60×10^{-20}.

I get from Bridgman, as the value of the Thomson effect at normal pressure, $\sigma = -3.20T$. Thus the K_2 of my Eq. (5), the B of Eq. (9), is zero, and so, according to Eq. (8), $C_2 = 0$.

The K_1 of Eq. (5), the A of Eq. (9), is -3.20, and so by means of Eq. (7) I get $C_1 = -79.86\times 10^{-6}$, instead of the -80.4×10^{-6} given above.

With these values of C_2 and C_1, I get from Eq. (10) $C = 0.1885$, instead of 0.19.

Accordingly I now have, as the normal values of the characteristic constants in bismuth,

q	s	(λ_c'/R)	C	$C_1\times 10^6$	C_2
1.20	4.35	790	0.1885	-79.86	0

The value of σ yielded by Bridgman's observations on bismuth under a given high pressure will, in the manner just illustrated, give three of the six equations needed for determining the values of the characteristic constants under this pressure, as will presently be seen; but I have not yet quite done with the normal state.

I wish to call especial attention to the fact that the normal values of the constants, as last given above, are in accord with the experimentally known values of electric and thermal conductivity. To do this I take Eq. (20) and, using therein the known value of the electric conductivity, together with such of the "constants" as are needed, I calculate from this equation the value of θ, the thermal conductivity, for 0°, 30°, and 100°C. I thus get $\theta=0.02021$, $\theta_{30}=0.01909$, $\theta_{100}=0.01656$. Jaeger and Diesselhorst give $\theta_{18}=0.0194$, $\theta_{100}=0.0161$. I regard this degree of accord between calculated and observed values as satisfactory for the present, but I must take care not to be misunderstood. I have not calculated θ by means of quantities determined entirely without reference to θ, I have merely found it practicable to select "characteristic constant" values which are for the most part in good agreement, numerically, with the known values of the electric conductivity, the thermal conductivity and the thermoelectric qualities of the various metals dealt with.

The value of θ_{30}, as calculated by means of my constants used in Eq. (20), is of especial importance here, as the observations of Bridgman on the value of θ under pressure were all made at or near 30°C. He measured merely relative *changes* of θ, and to get, for high pressures, definite values of θ_{30}, such as are given in the last column of the table above, I have applied his pressure coefficients of θ-change, at 30°C, to the value of θ_{30} as found above for normal pressure. The value of θ_{30} thus found for any given pressure will, when used as the first member of Eq. (20), make this equation available as the fourth of the six needed for determining the values of the characteristic constants under the given pressure.

We need two more equations, and we get them from the changes of the Peltier effect, under pressure, at 0°C and 75°C (100°C for all metal except bismuth), respectively. They are of the same type as the Peltier effect equation already written, without number, in the first part of this paper. The subscript α indicating uncompressed metal and the subscript β compressed metal, they are

$$[(k_f/k)_\beta\lambda_\beta=(k_f/k)_\alpha\lambda_\alpha+\Pi_{\alpha\beta}]_0, \tag{21}$$

and

$$[(k_f/k)_\beta\lambda_\beta=(k_f/k)_\alpha\lambda_\alpha+\Pi_{\alpha\beta}]_{100}. \tag{22}$$

Values of $\Pi_{\alpha\beta}$ are given in the table of data which precedes. Values of $(k_f/k)_\alpha\lambda_\alpha$ can be found from the values of the normal characteristic constants, and thus the values of $(k_f/k)_\beta\lambda_\beta$ are determined.

Our task is now to find values of the characteristic constants that will satisfy the six equations indicated, under some chosen high pressure. For bismuth I shall take $p=2000$ kgm/cm².

The value of σ in this case is the same as at normal pressure; that is, $\sigma=-3.20T$, and therefore I know at once that $C_2=0$; but it is not safe to assume from this that the characteristic constants, as a whole, remain unchanged. My method of procedure is to select, after a general survey of the conditions to be satisfied, tentative values of q, s, and (λ_c'/R), and then by trial find whether they will serve. Giving my readers at once the benefit of many hours spent in experimentation, I put $q=1.1974$, $s=4.27$, $(\lambda_c'/R)=787.28$. Then I get from Eq. (7) $C_1=-81.221\times10^{-6}$, and from (10) $C=0.18914$.

Put into Eq. (20) these values of my constants give $\theta_{30}=0.17906$, the mark aimed at being 0.1790. This is satisfactory, for I know from trial that a still closer adjustment could be made by means of a slight change in the value of s without change of q or of λ_c'.

Put into Eqs. (21) and (22) they give at 0° $\left(\frac{k_f}{k}\right)_\beta \lambda_\beta=3.1828\times10^6$, for 3.1828×10^6, and at 100° $\left(\frac{k_f}{k}\right)_\beta \lambda_\beta=3.5853\times10^6$, for 3.5858×10^6.

This will do, though I should like to have the difference less in the last case. I do not attempt closer adjustment, for I know that any change which would eliminate this difference would very likely introduce an equally serious difference in the preceding case, for 0°C. It would doubtless be possible to find by trial values of q, s, and λ_c' that would reduce the difference to zero, in the 4th decimal place, at both 0° and 100°; but it would probably take several hours of painstaking logarithmic calculations to reach this result. If it is asked why so much pains should even be thought of in such a case, the answer is that very slight adjustments needed to eliminate the differences at *both* 0° and 100° simultaneously may require very appreciable changes in the values of both q and λ_c'. In fact, the question whether q increases or decreases or remains unchanged under the given pressure may find its answer in a careful adjustment of differences in the 4th place of decimals in the values of $\left(\frac{k_f}{k}\right)_\beta \lambda_\beta$. In most metals the value of $\Pi_{\alpha\beta}$ is much smaller than it is in bismuth, and in many cases I have worked diligently in the 5th place of decimals, not because I regard the precise values of the constants q, s, etc., important, or even ascertainable, but because I think the *changes* which these constants undergo under pressure may prove to have considerable significance.

In attempting to deal with bismuth under a pressure of 4000 kgm. per sq. cm. I have had no success. In this case the value of σ, according to Bridgman's observations, while retaining its first term unchanged, develops a rather large second term, $-0.02tT$, and when I apply my mathematical apparatus everything turns topsy-turvy. In order to avoid getting a negative value for C, which is merely the ratio (k_f/k) at C0° and therefore must be positive, I am obliged to jump the value of q from 1.2 to something above 1.5, and even so I am not able to meet the other conditions imposed by my data. The fact is, as I have already said, that in such a case the value of σ is not accurately expressed even by a two-term formula, and it may well be that in this condition of things the assumptions on which I have based my Eqs. (7), (8) and (10) break down.

The other metals I shall discuss here in a much more summary fashion, reserving for Table II values which I have found for the characteristic constants at high pressures.

COPPER

For copper, with the somewhat revised normal values of the characteristic constants, σ being $-0.966T$, I get by use of Eq. (20)

$$\theta_0=0.9355, \quad \theta_{30}=0.9110, \quad \theta_{100}=0.8684.$$

Jaeger and Diesselhorst found $\theta_{18}=0.918$, $\theta_{100}=0.908$.

IRON

Iron is at the best a bad metal to deal with here, for even at normal pressure the value of σ has a large second term, being $(1.78+0.516\ t)T$. The somewhat revised normal constants (see Table II) give $\theta_0=0.1669$, $\theta_{30}=0.1610$, $\theta_{100}=0.1607$. This succession of θ values seems improbable, though it is doubtful whether the conductivity of iron is known by experiment with sufficient accuracy to show conclusively that the series is incorrect. Jaeger and Diesselhorst give $\theta_{18}=0.161$ and $\theta_{100}=0.151$ for "pure iron." I regard my own calculated values as unsatisfactory, and I doubt whether my theory, in its present form, can deal quite successfully with any metal in which the value of σ has a large second term.

NICKEL

Nickel is much more tractable than iron, having a one-term value of σ, $3.56T$, under normal pressure and an equally simple value, $3.542T$, under a pressure of 4000 kgm/cm^2. The revised normal values of the characteristic constants give $\theta_0=0.1429$, $\theta_{30}=0.1409$, $\theta_{100}=0.1352$. Jaeger and Diesselhorst give $\theta_{18}=0.142$, $\theta_{100}=0.138$.

PLATINUM

The normal values of the characteristic constants give $\theta_{30}\equiv0.1675$, $\theta_{30}=0.1682$, $\theta_{100}=0.1710$.

These values of θ agree with those found by Jaeger and Diesselhorst in showing an increase with rise of temperature but indicate a smaller coefficient of increase. Jaeger and Diesselhorst give $\theta_{18}=0.1664$, $\theta_{100}=0.1733$.

SILVER

This is a peculiarly well-behaved metal. All the way up to a pressure of 12000 kgm/cm^2 it keeps a one-term value of σ. For normal pressure my formula (20) gives $\theta_0=1.027$, $\theta_{30}=1.008$, $\theta_{100}=0.9705$, whereas Jaeger and Diesselhorst give $\theta_{18}=1.006$, $\theta_{100}=0.992$.

TIN

Tin was not a well-behaved metal in Bridgman's tests. He had experimental difficulties with it, the pressure coefficient of thermal conductivity proved to vary in a marked way, diminishing with increasing pressure; the Thomson coefficient σ, beginning as a one-term quantity, at normal pressure, developed a second term at 2000 kgm/cm^2, and this second term, small to be sure, is negative, $-0.000025\ tT$, if derived from σ_0 and σ_{50}, while it is positive, $+0.000019\ tT$, if derived from σ_0 and σ_{50}.

At normal pressure I get $\theta_0=0.1573$, $\theta_{30}=0.1526$, $\theta_{100}=0.1437$. Jaeger and Diesselhorst give $\theta_{18}=0.155$, $\theta_{100}=0.145$.

Taking the case $p=2000$ kgm/cm^2, but using Bridgman's mean pressure-coefficient of θ, $+0.0_4122$, found from the whole range of pressure up to 12000, I get, from the value of θ_{30} given above, 0.1563 as the value to be yielded by Eq. (20). I take $\sigma=(0.13508+0.0_819\ t)T$. On this basis I get the set of values given on the line beginning Tin $2000_{(1)}$ in Table II.

Taking again the same case, I now undertake to estimate, by means of a curve given by Bridgman for one specimen of tin, the mean value of the pressure-coefficient of θ over the range from 0 to 2000 kgm/cm^2. I thus find the value 0.0_42016, and with this, applied to the value of θ_{30} at normal pressure, I get 0.1587 as the value to be given by Eq. (20). On this basis I find the set of values given on the line beginning Tin $2000_{(2)}$ in Table II.

ZINC

Zinc, for which Bridgman gives a one-term value of σ, $0.99T$, at normal pressure, is peculiar in showing a two-term value at 2000 kgm/cm^2 and again a one-term value, $0.981T$, at 4000. Therefore I pass over the case of lower pressure and take that of the higher.

For the normal condition I get $\theta_0=0.2670$, $\theta_{30}=0.2645$, $\theta_{100}=0.2583$. Jaeger and Diesselhorst give $\theta_{18}=0.2653$, $\theta_{100}=0.2619$.

DISCUSSION OF RESULTS

I have evaluated in at least one case for each of the eight metals under consideration the change of characteristic constants produced by high pressure, and the numerical results of my study are brought together in Table II. Looking over this Table, we see that in five of the eight metals pressure decreases slightly the value of q. This means that in these five metals increase of pressure apparently decreases slightly the rate of ionization accompanying rise of temperature. In copper and silver, however, an increase of q is indicated; in iron no change. I am unable at present to comment profitably on these varieties of behavior with respect to q.

TABLE II

Changes of qualities and "characteristic constants" under pressure

	$p\left(\frac{k\,\text{gm}}{\text{cm}^2}\right)$	q	s	λ_c'/R	$C\times10^2$	$C_1\times10^6$	$C_2\times10^8$	P_k	P_θ
Bismuth	0	1.20	4.35	790	18.85	−79.9	0	−	—
	2000	1.1974	4.27	787.3−	18.91	−81.2	0		
Copper	0	1.49	6.80	43.7	6.75	−16.5	0	+	−
	2000	1.4902	6.677	42.91	6.87	−16.8	0		
Iron	0	1.20	15.0	98	1.99	12.03	19.8	+	−
	2000	1.20	14.93	97.3	1.999	11.6	20.1		
Nickel	0	1.60	5.0	128	13.09	84.3	0	+	−
	4000	1.594	4.764	121.3	13.74	88.0	0		
Platinum	0	1.60	6.24	131.7	8.02	50.05	0	+	−
	2000	1.583	6.22	126.0	8.07	49.3	0.845		
Silver	0	1.49	7.1	49.3	6.57	−14.1	0		
	4000	1.4902	6.915	47.71	6.74	−14.7	0	+	−
	8000	1.4904	6.740	46.27	6.91	−15.2	0		
	12000	1.4906	6.560	44.98	7.09	−15.7	0		
Tin	0	1.51	6.66	274	6.47	2.34−	0		
	2000 (1)	1.5098	6.68	278.6	6.44	2.34+	0.0165	+	+
	2000 (2)	1.5099	6.77	282.3	6.36	2.31−	0.0163		
Zinc	0	1.55	7.00	170	6.07+	16.5	0		
	4000	1.5496	6.96	168.9−	6.07−	15.0	0	+	+

Of more obvious importance is the fact that seven of the eight metals, all except tin, show a decrease of both s and (λ_c'/R) under pressure. This means, as reference to Eq. (3) will at once show, that the heat of ionization within the metal is decreased by increase of pressure. This outcome of the examination to which I have submitted Bridgman's data was expected. The verification of this surmise has, I venture to think, some interest as bearing on the question whether the theory of heat conduction which is now an integral part of my general "dual theory" is on the whole illuminating and helpful. The old puzzle as to why thermal conductivity, evidently connected closely in some way with electric conductivity, changes but little with rise of temperature while thermal conductivity falls off rapidly, I dealt with years ago in assigning to the s of Eq. (3) such values, in the individual metals, as would account, approximately at least, for the discrepancy noted.[21] But now Bridgman's pressure experiments have revealed a new puzzle in the relations of thermal conductivity and electric conductivity. Examination of the last two columns of Table II, in which P_k means pressure-coefficient of electric conductivity while P_θ means pressure-coefficient of thermal conductivity, shows that in five of the eight metals these coefficients have opposite signs. Moreover, in bismuth, both coefficients being negative, P_θ is numerically greater than P_k, a fact indicated here by the difference in size of the two negative signs. In tin, both being positive, P_θ is greater than P_k, while in zinc, both again being positive, P_k is the greater.

Will the same general conception which has taken care of the difference in temperature coefficients of k and θ account, without new hypotheses, for the differences in the pressure coefficients of these two conductivities? Putting aside for the moment the case of tin, we can say, yes. In copper, iron, nickel, platinum, and silver, electric conductivity increases under pressure, while thermal conductivity decreases. The main thing we have to do to explain this difference of behavior is to suppose that within these metals occur the changes of s and λ_c' shown against these metals respectively in Table II. In each of these five metals the changes of s and λ' are such as to reduce the heat of ionization, and, as I have already indicated, a diminution of the heat of ionization under pressure is so consistent with my previous conceptions that, before examining the experimental evidence in the case, I declared my expectation of finding it. (But see footnote.[22])

In bismuth and in zinc also the indicated changes of s and of λ_c' are such as to require a decrease of the heat of ionization with increase of pressure. Tin is the only one among the eight metals in which the

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[21] Eq. (20) shows $k_a k_f/k$ as a factor of θ. If we suppose each of the k's to decrease by the same proportional amount, say n percent, with a given rise of temperature, which is approximately true, θ would in consequence suffer the same percent decrease if it were not for the counteracting influence of the heat of ionization factor, $(\lambda_c'/R+s\ T)$.

[22] It must be admitted that the decrements of λ which I here find with increase of density are far too small to encourage the idea that the temperatures changes I have assumed for λ, in assigning values of s to the various metals at normal pressure, can be accounted for by the changes of density due to changes of temperature. If I am to keep these values of s, and so continue my endeavor to make my "cyclic" electric currents carry the whole burden of thermal conduction, it seems necessary to hold that increase in the range of thermal agitation may directly increase λ.

opposite change appears, and tin, it has already been said, was a peculiarly troublesome and uncertain metal in Bridgman's experiments.

The fertility of this conception, the importance of the part played by the latent heat of ionization, is worthy of further illustration. We have looked up the temperature scale from 0° to 100°C. If we look down this scale, how are we to account for the fact that, in spite of the immense increase of electric conductivity at very low temperatures, thermal conductivity does not have any corresponding increase there? Is there not something luminous and satisfying in the idea that heat of ionization is a necessary factor in heat conduction and that this factor, in accordance with the theory of this paper and in accordance with the "third law" of Nernst, tends to vanish or to become very small at low temperatures?

Again, how shall we explain the general tendency of Peltier effects toward extinction at low temperatures? Here too, according to the conceptions and the formulas of this paper, latent heat of ionization is a vital factor, and so there is no mystery in the observed temperature change. It is true that the ordinary conception of the Peltier effect heat, as due to the expansion of the free electron gas in going from one metal to another, accounts for the diminution of this heat with fall of temperature; but this conception cannot account for Bridgman's discovery of internal Peltier heat within a metal crystal.

The mathematical expression of the Peltier effect, in my theory, being

$$\Pi_{\alpha\beta} = (k_f/k)_\beta \lambda_\beta - (k_f/k)_\alpha \lambda_\alpha ,$$

pressure may act upon it either through the (k_f/k) factor or through the λ factor. Taking, for simplicity, the temperature as 0°C, which makes $(k_f/k) = C$, we have

$$\Pi_{\alpha\beta} = C_\beta \lambda_\beta - C_\alpha \lambda_\alpha .$$

It is to be remembered that, in the cases we are here dealing with, α indicates the natural state and β the compressed state of the same metal. Examination of Table II shows that in all of our eight metals except tin and zinc C_β is greater than C_α, which fact tends to give $\Pi_{\alpha\beta}$ a positive value. But examination of Table I shows that in all of the eight metals except iron and tin $II_{\alpha\beta}$ at 0° is negative. That is, in five of the eight metals the sign of $\Pi_{\alpha\beta}$ at 0° is determined by the effect of pressure on λ, not by the effect on C. In all of the metals the value of $\Pi_{\alpha\beta}$ at 100° is negative, though in only two of them, tin and zinc, is $(k_f/k)_\alpha$ greater than $(k_f/k)_\beta$ at this temperature. In a majority of cases, then, the net effect of pressure on the Peltier effect comes through the λ factor, in opposition to the effect produced through the (k_f/k) factor.

But the effect of pressure on the ratio (k_f/k) deserves some further comment. A few years ago I was of the opinion that the "free" electrons moved through the spaces between the atoms, and so I believed that pressure, bringing the atoms nearer together, would tend to lessen k_f while it would probably increase k_a, the associated electron conductivity. I took it for granted, therefore, that (k_f/k) would be diminished by pressure. But of late we have become familiar with the idea that slow-moving electrons may pass through atoms. The fact that most of the cases I have studied in this paper indicate an increase of (k_f/k) with increase of pressure is favorable to this conception. If we adopt it and then reflect that decrease of temperature tends to extinction of λ,—that is, to extinction of the difference between "free" electrons and "associated" electrons,—we may come to think of the "supra-conductive" state as one in which the metal is, as regards the conductive electrons, in a state of flux.

In a note too long to be added here it is shown that, according to the indications of the dual theory under discussion, the work done against opposing forces in photo-electric emission should be nearly independent of temperature, whereas the work done against opposing forces in thermionic emission should be $(b-aT)$, where b and a are positive constants. This suggests the following transformation of Richardson's emission formula

$$i=AT^{1/2}\epsilon^{\frac{-b_0}{T}}=AT^{1/2}\epsilon^{-a}\epsilon^{\frac{aT}{T}}\epsilon^{\frac{-b_0}{T}}=A'T^{1/2}\epsilon^{\frac{-(b_0-aT)}{T}}.$$

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