AN EXTENSION OF THE ELECTRON THEORY OF METALS. I. THERMOELECTRICITY AND METALLIC CONDUCTION.

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Synopsis.—Using as a starting-point the simple equations deduced from the electron theory by J. J. Thomson and others for thermo E.M.F., thermoelectric power, Peltier E.M.F. and the Thomson effect, and assuming that the number of free electrons in unit volume of a metal is an exponential function of the temperature, the author shows that (1) the thermoelectric power is a linear function of the temperature, (2) the equations relating thermo E.M.F. and temperature, and Peltier E.M.F. and temperature, represent parabolas having their axes perpendicular to the axis of temperature, and (3) the Thomson effect is different for different metals and may be either positive or negative, but will usually have a positive temperature coefficient. Likewise, using the equations for electrical and thermal conductivity and making the second assumption that the number of positive centers with which the electrons collide changes with the temperature (these centers being atoms, molecules or clusters of molecules), it is found that (4) the electrical conductivity of pure metals decreases with increase of temperature but is not exactly inversely proportional to the absolute temperature, (5) the peculiar behavior of the electrical resistance of alloys can be accounted for, and (6) the thermal conductivity may either increase or decrease with the temperature, the temperature coefficient depending both upon the temperature and the material. A third assumption, viz., that the positive centers take part in the conduction of heat but not of electricity, leads to the conclusion that (7) the usual value deduced for the Wiedemann-Franz-Lorenz ratio is too small, and the variations in the value of this ratio at ordinary temperatures is accounted for. The above theoretical results, especially (1), (2) and (3), are, at least within the ordinary range of temperatures, in substantial agreement with experiment, since the constants involved in the theory can be determined from experimental data, and so the author concludes that (8) the concentration of electrons in a metal is an exponential function of the temperature, and (9) the number of positive centers changes with the temperature, the exact relation being somewhat uncertain. The number, however, must generally increase with the temperature.

Contents.

I. Introduction.

THE theory outlined in this paper is an attempt to amplify, or expand, the electron theory of metals as applied to thermoelectricity and metallic conduction so as to bring it more nearly into harmony with the experimental facts without at the same time doing violence to such portions of the theory as are not treated here. Three simple assumptions, relating the electrons, molecules and temperature, are made which will be studied in detail later. Certain mathematical forms are employed to express the assumed relations. It is not claimed that these expressions are more than first approximations to the true functions, neither is it claimed that they are even first approximations in the neighborhood of the absolute zero and temperatures near which marked changes in the structure of the material occur. It is claimed, however, that the theory presented here offers, at least within the range of ordinary temperatures, as good an explanation of the experimental facts here treated as previous theories do, and it explains some facts which have been unaccounted for hitherto.

At the outset the writer wishes to state that much of such merit as the present paper possesses is due to the fact that he has had the advantage of constant consultation with his colleague, Professor W. P. Boynton, whose familiarity with the kinetic theory of matter has made his numerous suggestions and criticisms of primary importance.

Throughout this discussion the symbols employed have the following meanings:

m = mass of an electron,
u = "mean square velocity" of the electrons,
T = absolute temperature,
t = Centigrade temperature,
α = the gas constant for a single electron, being defined by the equation $\frac{1}{2}mu^2 = \alpha T$,
ϵ = charge on an electron,
λ = mean free path of the electrons,
N = number of free electrons in one c.c. of a metal,
n = number of positive centers in one c.c. of a metal,
P = Peltier E.M.F.,
Q = thermoelectric power,
E = thermo E.M.F.,
σ = Thomson E.M.F., or so-called "specific heat of electricity,"
κ = electrical conductivity,
ρ = electrical resistivity, and
k = thermal conductivity.

The other symbols used are constants whose significance is obvious from the context. The subscripts 1 and 2 are used to refer to two different metals except where some other convention is specifically stated.

A theory to be completely satisfactory should account for the following facts.

1. The thermo E.M.F. between any two metals can usually be expressed by an equation of the form $E = At + \frac{1}{2}Bt^2$.

2. Similarly, the thermoelectric power of any two metals can usually be represented by a equation of the form $Q = A + Bt$.

3. The Peltier E.M.F. must satisfy the equation $P = QT$.

4. The Thomson effect may be either positive or negative and is different for different metals.

5. The Thomson effect has a temperature coefficient.

6. The electrical conductivity of pure metals at ordinary temperatures is almost inversely proportional to the absolute temperature, or the resistivity is nearly proportional to the absolute temperature. Usually the resistivity increases somewhat more rapidly than the absolute temperature.

7. At ordinary temperatures the electrical conductivity of alloys is frequently nearly independent of the temperature and occasionally increases with increase of temperature.

8. The thermal conductivity of a number of metals is nearly constant at ordinary temperatures and may either increase or decrease as the temperature is raised.

9. The ratio of the thermal to the electrical conductivity at all ordinary temperatures is nearly the same for all metals, the ratio being nearly proportional to the absolute temperature. In the case of pure metals the ratio usually increases somewhat faster than the absolute temperature, but in the case of alloys it usually increases more slowly.

Besides the facts just enumerated which are explained in the present paper there are number of galvanomagnetic, thermomagnetic and electronic emission phenomena which must ultimately be explained. No attempt is made to account for these effects, their treatment being reserved for a subsequent paper. So far as known none of the hypotheses advanced here in any way interferes with the explanation of any of these effects.[1]

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[1] For general discussions of the above phenomena, including the subject matter of the present paper, the reader is referred to J. J. Thomson's Corpuscular Theory of Matter, p. 49 et seq.; O. W. Richardson's The Electron Theory of Matter, p. 407 et seq.; E. Bloch's La Théorie Electronique des Métaux (in a series of essays published under the title Les Idées Modernes sur la Constitution de la Matière, Villars, Paris); K. Baedeker's Die Elektrischen Erscheinungen in Metallischen Leitern (Braunschweig); also N. R. Campbell's Modern Electrical Theory, pp. 54–86.

2. Previous Theories and Their Limitations.

The equations deduced from the electron theory by Sir J. J. Thomson, and which are taken as a starting-point in the present discussion, are:

$$P_{12} = \frac{2\alpha T}{3\epsilon} \log \frac{N_1}{N_2}, \tag{1}$$

$$Q_{12} = \frac{2\alpha}{3\epsilon} \log \frac{N_1}{N_2}, \tag{2}$$

$$\sigma = \frac{2\alpha}{3\epsilon} \left\{ T \frac{d}{dT} (\log N) - \frac{1}{2} \right\}, \tag{3}$$

$$\kappa = \frac{\epsilon^2 N \lambda u}{4 \alpha T}, \tag{4}$$

and

$$k = \tfrac{1}{3}\, \alpha N \lambda u. \tag{5}$$

From equations (4) and (5) we obtain the Wiedemann-Franz law that the ratio k/κ is a constant for all metals at any given temperature and the Lorenz law that this ratio is proportional to T, which laws together give

$$\frac{k}{\kappa T} = \frac{4}{3} \left(\frac{\alpha}{\epsilon} \right)^2. \tag{6}$$

The thermoelectric equations satisfy the following equations which were deduced from thermodynamical considerations by Lord Kelvin, namely,

$$P = QT, \tag{7}$$

and

$$\sigma_1 - \sigma_2 = T \frac{dQ_{12}}{dT}. \tag{8}$$

The constant multiplying factors on the right-hand side of equations (1) to (5), inclusive, have been given different values by different theorists, but in any case they only differ by simple numerical factors. Thus Drude[1] replaces $2\alpha/3\epsilon$ by $4\alpha/3\epsilon$ in equations (1), (2) and (3), and Lorentz,[2] assuming the Maxwellian distribution of velocities among the electrons, finds instead of equation (4) the equation

$$\kappa = \sqrt{\frac{2}{3\pi}} \left(\frac{\epsilon^2 \lambda N u}{\alpha T} \right), \tag{4a}$$

and instead of equation (5) the equation

$$k = \frac{8}{9} \sqrt{\frac{2}{3\pi}} (\alpha N \lambda u). \tag{5a}$$

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[1] Ann. Phys., 1, 566, 1900 and 3, 369, 1900.

[2] Lorentz, The Theory of Electrons, pp. 63–67.

From (4*a*) and (5*a*) it follows that

$$\frac{k}{\kappa T}=\frac{8}{9}\left(\frac{\alpha}{\epsilon}\right)^2. \tag{6a}$$

The value of the ratio $k/\kappa T$ thus found is but two thirds of that found from the simple theory by Thomson and Drude. Since these differences in multiplying constants are of only secondary importance in connection with the present discussion they will be disregarded for the present. It may be remarked, however, that experimental data may, with the aid of the theory presented in this paper, enable one to discriminate between the different methods of approach to the problem and to select that one which agrees best with experiment.

It has usually been assumed either that N remained constant or else was either directly or inversely proportional to the square root of the absolute temperature. The first assumption was made in order to explain the optical properties of metals, the second was made by J. J. Thomson to account for the Thomson effect, and the last was made to account for the fact that at ordinary temperatures the temperature coefficient of resistance of a number of metals is approximately equal to 1/273 per Centigrade degree. From equation (4) it follows that if the electrical conductivity is inversely proportional to the absolute temperature, either N or λ must be inversely proportional to the square root of the absolute temperature, since $u = \sqrt{2\alpha T/m}$. We see no reason why λ should vary to any appreciable extent if the number of molecules does not change and the alteration in volume is quite small. Then N must change with temperature. But from the optical properties of metals it seems that N does not change.[1] So one has his choice: either N changes or it does not. But whether N is constant or is proportional to some power of the absolute temperature, the proportionality factor depending upon the material, certain results follow which are not in harmony with experiment. Some of these discrepancies are:

1. The thermo E.M.F. is a linear function of the temperature.
2. The thermoelectric power is constant for any given pair of metals.
3. The Thomson effect is the same for all metals at all temperatures.
4. The thermal conductivity of any metal is independent of the temperature.
5. The ratio $k/\kappa T$ is the same for all metals at all temperatures and within the range of ordinary temperatures is usually too small.

On the whole, the most that can be said for the theories so far published is that they show that these properties are to be expected, but they are wholly inadequate when it comes to quantitative measurements.

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[1] Drude, Ann. Phys., 14, 951, 1904.

3. Statement of the New Theory.

The fundamental assumptions upon which this theory is based are

(1) That the number of free electrons in a metal *changes* with the temperature,

(2) That the number of positive centers with which the electrons collide, whether these centers are atoms, sub-atoms, molecules or groups of molecules, *changes* with the temperature, and

(3) That these positive centers take part in the transfer of heat but not of electricity.

The mathematical forms which have been selected to express the relations between the numbers of electrons and positive centers are

$$N = ae^{xT}, \tag{9}$$

and

$$n = be^{yT} \tag{10}$$

where a and b are positive constants, and nothing is postulated regarding the signs of x and y.

We are led to the first assumption by the fact that unless equations (1), (2) and (3) are entirely wrong, N must depend upon T. The exponential form of equation (9) is suggested by the logarithmic form of these three equations. The excellent agreement of the resulting equations with experiment indicates the probability that equation (9) is an accurate representation of the facts.

The assumption that the number of positive centers with which the electrons collide changes with the temperature is somewhat startling.[1] For our purposes it is unimportant whether these centers are atoms, sub-atoms, molecules or clusters of molecules. A great deal of uncertainty exists as to the states of aggregation in solids and liquids, and there is no *a priori* reason why the state of aggregation in a substance should not vary with the temperature of the substance. It is not necessary that all the centers shall be alike. A continual process of disintegration and recombination of the centers may be going on. If a theory based on this assumption should harmonize better with experiment than others, this circumstance would lend color to the assumption.

Remembering that, as in the kinetic theory of gases, $\lambda = f/nr^2$, where r is the radius of the positive centers and f is a constant, and substituting be^{yT} for n in equation (10), we obtain

$$\lambda = ce^{-yT}, \tag{11}$$

where $c = f/br^2$.

When $T = 0$, $N = a$, $n = b$ and $\lambda = c$. But when $T = \infty$, then

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[1] Cf. Richardson's The Electron Theory of Matter, p. 467.

N and n are both infinite, and $\lambda = 0$. In practice, of course, T never approaches infinity, and since both x and y prove to be small, the values of N and n at, say, 2000° C. will probably seldom exceed 50 to 100 times the corresponding values at the absolute zero.

The third assumption seems reasonable from the fact that insulators conduct heat even though they do not conduct electricity, and have very few, if any, free electrons.

The only assumption involved in the theory of thermoelectricity here presented is the first, namely, that the number of free electrons is a function of the temperature. The second assumption is introduced to account for electrical conductivity, namely, that the number of positive centers is a function of the temperature. The third assumption, that the positive centers take part in the conduction of heat, is involved only in those portions of the theory which deal with thermal conductivity.

Equations (1) to (5), inclusive, are taken as the starting-points in the present discussion. This is not to be interpreted as indicating a preference on the part of the writer for one physicist's theory rather than that of another. In the light of our present knowledge, however, it seems that these equations are likely to be as valid as any of the others. Changing the constant factors has no effect upon the qualitative results of the theory presented here, and only to a minor extent upon the quantitative results.

4. PELTIER E.M.F.

Sir J. J. Thomson obtained equation (1) given above for the Peltier E.M.F. by assuming that electrons under the influence of an electric force flow across the boundary between two metals until the electric force is in equilibrium with the opposing pressure gradient at the boundary. The expression for the Peltier E.M.F. on the basis of the present extension of the simple theory is readily obtained by substituting in equation (1) the values of N_1 and N_2 given in equation (9), namely, $N_1 = a_1 e^{x_1 T}$ and $N_2 = a_2 e^{x_2 T}$. This gives

$$P_{12} = \frac{2\alpha T}{3\epsilon}\left\{\log\frac{a_1}{a_2} + (x_1 - x_2)T\right\}. \tag{12}$$

This equation may be rewritten in the form

$$P = AT + BT^2, \tag{12a}$$

or

$$P = P_0 + (273B + Q_0)t + Bt^2, \tag{12b}$$

where

$$A = \frac{2\alpha}{3\epsilon}\log(a_1/a_2),\ B = \frac{2\alpha}{3\epsilon}(x_1 - x_2),\ Q_0 = A + 273B,\ P_0 = 273Q_0,$$

and $t = T - 273$. P_0 is the Peltier E.M.F. at 0° C. and, as we shall see in the next section, Q_0 is the thermoelectric power of the pair of metals at 0° C.

The equations (12), (12*a*) and (12*b*) represent a parabola with its axis perpendicular to the axis of temperature. We should expect the Peltier E.M.F. to have a maximum value at the absolute temperature.

$$T' = -A/2B, \tag{13}$$

or in Centigrade degrees,

$$t' = -A/2B - 273 = -(273B + Q_0)/2B. \tag{13a}$$

The value of the Peltier E.M.F. at the temperature T' should be

$$P' = -A^2/4B. \tag{14}$$

If we knew the experimental form of the parabola it would be possible for us to calculate the values of A and B, and from these values we could obtain the value of the ratio a_1/a_2 and also of the difference $(x_1 - x_2)$. In practice, however, it will be very much simpler to obtain these values from the thermo E.M.F.

5. Thermoelectric Power.

The equations for the thermoelectric power are readily obtained from the corresponding ones for the Peltier E.M.F. by dividing by T (see equation (7)). From equations (12), (12*a*) and (12*b*) we thus obtain

$$Q_{12} = \frac{2\alpha}{3\epsilon}\left\{\log\frac{a_1}{a_2} + (x_1 - x_2)T\right\}, \tag{15}$$

$$Q = A + BT, \tag{15a}$$

and

$$Q = Q_0 + Bt, \tag{15b}$$

where A, B and Q_0 have the same values as in the preceding section. These equations represent quite accurately, by a suitable choice of constants, the thermoelectric power of a thermocouple consisting of almost any pair of metals.

6. Thermo E.M.F.

The expression for the thermo E.M.F. is obtained from that for the thermoelectric power by integrating the latter with respect to T. If E is the thermo E.M.F. between two metals 1 and 2, when their junctions are at the temperature T_1 and T_2, then

$$E = \int_{T_1}^{T_2} Q\,dT,$$

whence

$$E = \frac{2\alpha}{3\epsilon}\left\{\left(\log\frac{a_1}{a_2}\right)(T_2 - T_1) + \frac{1}{2}(x_1 - x_2)(T_2^2 - T_1^2)\right\}. \tag{16}$$

If we put $T_1 = 0$ and $T_2 = T$, then equation (16) becomes

$$E = \frac{2\alpha}{3\epsilon}\left\{ T \log\frac{a_1}{a_2} + \frac{1}{2}(x_1 - x_2)T^2 \right\}, \tag{17}$$

where E is the thermo E.M.F. between two junctions at 0° and T° absolute, respectively. Equation (17) may be rewritten in the form

$$E = AT + \tfrac{1}{2}BT^2. \tag{17a}$$

Substituting $t + 273°$ for T_2 and 273 for T_1 in equation (16) we obtain

$$E = Q_0 t + \tfrac{1}{2}Bt^2, \tag{16a}$$

where E is the thermo E.M.F. between two junctions at 0° C. and t° C., respectively.

Equations (17), (17*a*) and (16*a*) represent a parabola with its axis perpendicular to the axis of temperature. The maximum value of E occurs at the neutral temperature, which is therefore given by the equation

$$T' = -A/B, \tag{18}$$

or

$$t' = -Q_0/B. \tag{18a}$$

The thermo E.M.F. of the couple when one junction is at 0° C. and the other is at the neutral temperature is given by the equation

$$E' = -Q_0^2/2B. \tag{19}$$

Experimentally it is found that the thermo E.M.F. between any two metals is quite accurately represented by a parabola with its axis perpendicular to the axis of temperature, that is, by equations of the type deduced above, where A and B may either positive or negative. Thus we see that the equations here deduced for thermoelectric power and thermo E.M.F. are in agreement with the experimental facts. And since equation (7) has been shown to be true both experimentally and theoretically, the equations for the Peltier E.M.F. must also be in agreement with the experimental facts. From our theory we see that A is positive or negative according as a_1 is greater or less than a_2. Similarly, B is positive or negative according as x_1 is greater or less than x_2.

From the known values of A and B obtained from experiment we may calculate the values of a_1/a_2 and $(x_1 - x_2)$ by means of the following equations:

$$a_1/a_2 = e^{3\epsilon A/2\alpha}, \tag{20}$$

and

$$x_1 - x_2 = 3\epsilon B/2\alpha. \tag{21}$$

It may be remarked in passing that if N were a constant different for different metals, or if N were proportional to any power of the absolute temperature, the proportionality factor being different for different metals, then the thermoelectric power would be constant and the thermo E.M.F. would be proportional to the difference between the absolute temperatures of the two junctions. These conclusions, however, are contrary to experiment.

7. Thomson Effect.

When we substitute ae^{xT} for N in equation (3) we obtain

$$\sigma = \frac{2\alpha}{3\epsilon}(Tx - \tfrac{1}{2}). \tag{22}$$

Since for practically all metals the absolute value of σ is considerably less than $\alpha/3\epsilon$, it follows that x must be positive. Hence, we may conclude that *in order to account for the Thomson effect it is necessary to assume that the number of free electrons in a metal increases with the absolute temperature.* So long as x is positive, σ will have the same sign as $(Tx - \tfrac{1}{2})$, and the absolute value of σ, when it is negative, cannot be greater than $\alpha/3\epsilon$. On the other hand, σ may have any positive value when x is positive. In the case of certain alloys[1] it appears that σ is negative and greater than $\alpha/3\epsilon$. In such cases x must be negative.

Differentiating equation (22) with respect to T, we obtain

$$\frac{d\sigma}{dT} = \frac{2\alpha x}{3\epsilon}. \tag{23}$$

From equation (23) it appears that *the Thomson effect has a temperature coefficient, and that this temperature coefficient is normally positive.* Qualitatively at least, this result is in harmony with some of the best experimental results such, for example, as those obtained by Berg[2] on copper. In the case of the alloys mentioned above, which have abnormally high negative values of the Thomson effect, Laws found that the temperature coefficients were negative. This is in harmony with our theory.

From the value of the Thomson effect at any temperature it is possible to calculate the value of x. Solving equation (22) for x we obtain

$$x = \frac{3\epsilon\sigma + \alpha}{2\alpha T}. \tag{24}$$

Generally speaking, Tx cannot be very far different from $\tfrac{1}{2}$ at ordinary temperatures, since σ is usually quite small in comparison with $\alpha/3\epsilon$. This being so, let us assume that $Tx = \tfrac{1}{2}$ and that $T = 300°$ absolute (27° C.). Then $x = 0.001667$. Substituting this value of x in equation

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[1] Laws, Phil. Mag., 7, pp. 560–578, 1904, and Caswell, Phys. Rev., N.S., XII., pp. 231–237, 1918.

[2] Ann. Phys., 32, pp. 477–519, 1910.

(9), we find the ratio of the value of N at any temperature $(T + 1)$ to its value at the temperature T to be 1.0017. Or, to use a somewhat larger temperature interval, the ratio of N at $(t + 100)^\circ$ C. to its value at t° C. is 1.181. For a temperature interval of 1000° C. the ratio is 5.294. Assuming 0.002 as a probably maximum value of x for a pure metal, we find the corresponding values of the ratio for a temperature interval of one degree Centigrade to be 1.0020, for a 100° C. interval 1.2214, and for a 1000° C. interval 7.389.

If our theory is correct, the Thomson effect is a linear function of the temperature which approaches the common value for all metals at the absolute zero of $\sigma = -\alpha/3\epsilon$. In case we should have used $4\alpha/3\epsilon$ instead of $2\alpha/3\epsilon$ in equations (1), (2) and (3), then σ should have a different limiting value. The same is true if any other factor is used instead of $2\alpha/3\epsilon$. If this limiting value of σ can be determined, then we have a means of selecting the best from among the different equations proposed.

It follows at once from equation (22) that

$$\sigma_1 - \sigma_2 = \frac{2\alpha T}{3\epsilon}(x_1 - x_2), \tag{25}$$

or

$$\sigma_1 - \sigma_2 = BT, \tag{25a}$$

these equations being in the form of equation (8). It is obvious that the metal having the more positive value of x will have the more positive value of σ, and *vice versa*. Consequently, if we were to arrange a series of metals in the order of the slope of the corresponding lines in a thermoelectric power diagram, the metals should also be arranged in the order of their Thomson effects at any given temperature.

8. Electrical Conductivity.

In the preceding sections the only assumption which has been employed is that the number of free electrons is a function of the temperature, and the satisfactory agreement between the theory and experiment seems to prove the wisdom of selecting the expression ae^{xT} to represent this number at any temperature T. No assumption was made as to the sign of x, but we have found that to account for the Thomson effect in most substances x must be positive. To this assumption we now add a second, namely, that the number of positive centers is a function of the temperature, and, in consequence, the mean free path of the electrons is a function of the temperature. Any discrepancies between theory and experiment which appear in this section must, therefore, arise not from the first assumption, but from the second.

Substituting the value of N from equation (9), the value of λ from equation (11), and $u = (2\alpha T/m)^{1/2}$ in equation (4), we obtain as the value of the electrical conductivity

$$\kappa = \frac{\epsilon^2 ac}{2\sqrt{2\alpha m}} e^{(x-y)T} \cdot T^{-1/2}, \tag{26}$$

which we shall rewrite in the form

$$\kappa = Ce^{-zT} \cdot T^{-1/2}, \tag{26a}$$

where $C = \epsilon^2 ac/2(2\alpha m)^{1/2}$, and $z = y - x$. Both C and z are constants for any given metal.

Since the electrical conductivity of pure metals within the range of ordinary temperatures is roughly inversely proportional to the absolute temperature, it follows from equation (26*a*) that the exponential factor on the right-hand side of the equation must decrease with increase of temperature. In order that this shall be so, z must be positive or $(x - y)$ must be negative. But since x is positive in the case of pure metals, y must also be positive and greater than x. Hence, we conclude that *in the case of pure metals both the number of free electrons in the metal and the number of positive centers with which they collide increases with the temperature, the number of positive centers, in general, increasing faster than the number of electrons.*

In the case of alloys the electrical conductivity cannot be said to bear any general relation to the temperature. In fact in the case of some alloys, such as manganin, the temperature coefficient is exceedingly small. In such cases the exponential factor may increase with the temperature. That is, if x is positive, then y is either positive and less than x or else y is negative, but if x should happen to be negative, as we have seen is probable in the case of some alloys, then y is also negative but numerically greater than x. The case when both x and y are positive seems the most likely to occur, since this is the rule for pure metals. In any case we may conclude that *in some substances, particularly alloys, the number of free electrons increases with the temperature faster than the number of positive centers with which they collide.*[1]

The electrical conductivity of carbon, which though not a metal conducts metallically, increases rather rapidly with the temperature. This means that z for carbon has a comparatively large negative value. This probably indicates a large positive value of x with a smaller positive, or possibly negative, value of y. An abnormally large value of x corre-

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[1] A good account of the electrical properties of alloys is given in Baedeker's Elektrischen Erscheinungen in Metallischen Leitern. Lord Rayleigh (Scientific Papers, Vol. IV., p. 232) has suggested that the resistance of alloys is unduly high owing to a "false resistance" arising from the Peltier effect between non-homogeneous parts of the metal.

sponds to an abnormally large positive value of the Thomson effect.

Since ρ is the reciprocal of κ it follows that

$$\rho = \frac{1}{C} e^{zT} \cdot T^{1/2}, \tag{27}$$

whence

$$z = \frac{1}{T}(\log C + \log \rho - \tfrac{1}{2} \log T). \tag{28}$$

If ρ is proportional to T, as is assumed but is not strictly true to fact, then

$$z = \frac{1}{T}(\log (CD) + \tfrac{1}{2} \log T), \tag{28a}$$

where ρ is put equal to DT.

From equation (28a) it appears that either ρ is not proportional to T or else z is not constant as assumed, but is a function of T. Whenever the value of z is greater than the right-hand side of equation (28a) the resistivity increases faster than the absolute temperature, but when the reverse is true the resistivity increases more slowly than the absolute temperature.

From equation (27) it is obvious that the resistivity of a metal approaches zero at the absolute zero, and increases continuously with the temperature providing z is positive. In case z is negative the resistivity should have a maximum value when $T = -(1/2z)$.

Since the factors a and c, which are contained in the value of C, are as yet undetermined, we cannot use equation (28a) to calculate the value of z. But since we know how ρ varies with T we may write

$$\frac{\rho_1}{\rho_0} = e^{z(T_1 - T_0)} \left(\frac{T_1}{T_0}\right)^{1/2}, \tag{29}$$

where ρ_1 and ρ_0 are the resistivities at $T_1°$ and $T_0°$ absolute, respectively. Putting $T_1 = T_0 + 1$, and solving for z, we obtain

$$z = \log \frac{\rho_1}{\rho_0} - \tfrac{1}{2} \log \left(1 + \frac{1}{T_0}\right). \tag{29a}$$

If we denote the temperature coefficient of resistance at T_0 by β, we may rewrite equation (29a) thus:

$$z = \log (1 + \beta) - \tfrac{1}{2} \log \left(1 + \frac{1}{T_0}\right), \tag{29b}$$

or as a first approximation which gives a result about one half per cent. too high

$$z = \beta - \frac{1}{2T_0}. \tag{29c}$$

We find the temperature coefficient of resistivity of copper given as 0.00428 at 18° C., *i. e.*, $T_0 = 291$, and so z is found to be 0.002545 if we use equation (29*b*), but is found to be 0.00256 if we use equation (29*c*).

From the ratio of the resistivities of two metals at any temperature T we may determine the ratio c_1/c_2, thus:

$$\frac{c_1}{c_2} = \frac{\rho_2 a_2}{\rho_1 a_1} e^{(z_1 - z_2)T}. \tag{30}$$

Since all the quantities on the right can be determined the ratio c_1/c_2 can be calculated. It should be noted, however, that the numerical values which we obtain for a_1/a_2, and consequently for c_1/c_2, depend upon whether we use $2\alpha/3\epsilon$ or some other multiplying factor in equations (1), (2) and (3).

9. Thermal Conductivity.

We now proceed to introduce the third assumption, namely, that the molecules or, more generally, the positive centers, whether these are atoms, sub-atoms, molecules or groups of molecules, take part in the transmission of heat, although they have no part in the transmission of electricity in solid bodies. In the simple equation (5), namely, $k = \frac{1}{3}\alpha N\lambda u$, N, λ and u refer specifically to the electrons. A fundamental assumption of the electron theory is the equi-partition of energy among the electrons and molecules, but there are certain reasons why we are at present unable to assign values to the molecular quantities corresponding to N, λ and u. Indeed for our present purpose it is unimportant whether such values can be assigned. Obviously, there is the probability that heat is transmitted by the molecules, or positive centers, by radiation as well as by conduction. What fraction of the total heat transmitted is transmitted by radiation we are unable to determine. For the present it remains an open question whether the equi-partition of energy law applies to the molecules or to the positive centers.

It is rather obvious that the mean free paths and the velocities of the positive centers, or of the molecules, will vary in the same directions as λ and u, respectively. We shall assume, for simplicity, that λ_1 is directly proportional to λ, and that u_1 is directly proportional to u, where λ_1 is the mean free path of the positive centers, or molecules, as the case may be, and u_1 is the corresponding mean square speed. We may then rewrite equation (5), substituting $N + n$ for N and introducing a constant ω which includes the proportionality factors connecting λ and λ_1, and u and u_1, and also the ratio of the total amount of heat transmitted by the molecules to that conducted by them. We thus obtain

$$k = \tfrac{1}{3}\alpha u\lambda(N + \omega n). \tag{31}$$

Equation (31) simply means that in view of our ignorance of the behavior of these positive centers, we feel justified in assuming that the fraction of the total heat transmitted by them is proportional to their number.

Replacing N by ae^{xT}, n by be^{yT}, λ by ce^{-yT} (see equations (9), (10) and (11)), and u by $(2\alpha T/m)^{1/2}$, equation (31) reduces to

$$k = \frac{\sqrt{2\alpha}}{3\sqrt{m}}\,ac\left(e^{(x-y)T} + \frac{\omega b}{a}\right)T^{1/2}. \tag{32}$$

It is at once apparent that in the case of pure metals the exponential factor in the first term on the right-hand side of equation (32) tends to make k decrease as T increases, since $(x - y)$ is negative, while the factor $T^{1/2}$ tends to make both terms increase as T increases. So k may either increase or decrease with increase in temperature.

10. THE WIEDEMANN-FRANZ AND LORENZ LAWS.

We have already seen that the Wiedemann-Franz law coupled with that of Lorenz leads to the relation that $k/\kappa T$ = *a constant*. Substituting the values of k and κ from equations (32) and (26), respectively, we obtain

$$\frac{k}{\kappa T} = \frac{4\alpha^2}{3\epsilon^2}\left(1 + \frac{\omega b}{a}e^{zT}\right). \tag{33}$$

When $\omega = 0$, this equation reduces to equation (6) as a special case. Equation (33) leads us to expect that the experimentally determined value of the ratio will always be greater than that calculated from the simple theory. Assuming the validity of equation (6), the experiments of Jaeger and Diesselhorst[1] on thirteen metals and three alloys gave values in every case, except that of aluminum, greater than we should expect from the simple theory; but if we assume the validity of equation (6*a*) the discrepancy is much greater, even aluminum being about thirty per cent. too high. It has been objected that the amount of heat transmitted by the positive centers, whatever they may be, must be much too small to account for the discrepancies between Jaeger and Diesselhorst's experiments and the simple theory. But this objection is based on the assumption that the heat so transmitted must be approximately the same as that transmitted by an insulator. This does not necessarily follow. If there are practically no free electrons in an insulator and there are large numbers of them in conductors, is it not reasonable to suppose that there may be more freedom of movement among the molecules in a conductor than among those in an insulator?

The minimum value which the right-hand side of equation (33) can have is $4\alpha^2(1 + \omega b/a)/3\epsilon^2$. This seems out of harmony with the results

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[1] Sitzungsber. Berlin, 1899, p. 719.

obtained by Meissner[1] at very low temperatures, since he found that for copper at 20° absolute the value of the ratio $k/\kappa T$ was but one seventh of its value at 0° C., the value at 0° C. being only slightly greater than $4\alpha^2/3\epsilon^2$.

If the subscripts 1 and 2 refer, respectively, to the temperature T_1 and T_2, then

$$\frac{k_2/\kappa_2}{k_1/\kappa_1} = \frac{\left(1 + \frac{\omega b}{a} e^{zT_2}\right) T_2}{\left(1 + \frac{\omega b}{a} e^{zT_1}\right) T_1}. \tag{34}$$

According to the simple theory this should be

$$\frac{k_2/\kappa_2}{k_1/\kappa_1} = T_2/T_1. \tag{34a}$$

Jaeger and Diesselhorst, working between the temperatures of 18° C. and 100° C., *i. e.*, between 291° and 373° absolute, found instead of the theoretical value of the ratio on the left-hand side of equation (34*a*), viz., $T_2/T_1 = 1.28$, that eight of the thirteen metals tested gave values greater than 1.28, two of them, platinum and palladium, giving values of 1.35, two gave values of 1.28, one of 1.27, one of 1.26 and one, bismuth, of 1.12. The three alloys tested gave results less than 1.28. Whenever y is greater than x, as we have seen is the case in pure metals, equation (34) leads us to expect the ratio to be greater than 1.28. In the majority of cases this seems to be true. But in the case of an alloy, such as manganin, which has a very small temperature coefficient of resistance, x is greater than y, and equation (34) leads us to expect the ratio to be less than 1.28. This is actually the case. In the case of manganin the ratio is 1.21.

11. Discussion of the Theory.

In this section the author wishes to make some general observations concerning the theory here presented. In the first place, we see that, since the equations are of the proper form and the values of the constants involved can be determined from experimental data, the agreement of the theory with the phenomena of the Peltier and Seebeck effects is not only qualitative but quantitative as well. Not only do the values of the constants so determined indicate that, in general, the number of free electrons increases with the temperature, but this is what we might expect, since the kinetic energy and, consequently, the agitation of the molecules increases with the temperature.

In a previous paper the author has shown that either (1) the electrons

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[1] Deutsch. Phys. Gesell., Verh. 16, 5, pp. 262–272, 1914.

which take part in thermoelectric phenomena are different from those which take part in electric conduction, or (2) the mean free path of the electrons in an alloy is noticeably different from that in a pure metal, one of the constituents of the alloy. The former statement seems unreasonable, while the latter is plausible if the formation of an alloy involves the regrouping of the atoms or molecules. Thus the writer was led to the conclusion that in some way a change is brought about in the mean free path of the electrons. The introduction of the exponential value of N from equation (9) into equation (4) makes the resulting change in the electrical conductivity in the opposite direction to that in which it actually occurs. So we have adopted the hypothesis that the mean free path of the electrons as well as their number is a function of the temperature. The change in the mean free path may be thought of as being brought about in either of two ways, always assuming that the number of collisions between electrons is negligible in comparison with the number between electrons and the positive centers. Either the size of the positive centers may change or their number. Assuming that the size changes but not the number we are led to conclusions which do not agree as well with experiment as do the conclusions which we arrive at by assuming that the number of positive centers is a function of the temperature. The author is inclined to believe that the exponential form of the function which has been employed in this paper is a fair representation of the facts, if temperatures near which marked changes in the structure of the metal occur, such as eutectic-points and melting-points, are excluded. In this connection it should be noted that the Peltier E.M.F. and the thermo E.M.F., both of which we assume depend only upon the concentration of the electrons, are not discontinuous functions of the temperature at the melting-point, but it appears that the electrical conductivity of a metal changes markedly as it passes from the solid to the liquid state. In the case of a number of metals, *e. g.*, cadmium, lead, potassium, sodium, tin and zinc, the electrical conductivity in the solid state at the melting-point is about one half the value in the liquid state at the same temperature. Exceptions are bismuth and antimony. In both of these the conductivity is approximately doubled as the substances passes from the solid to the liquid state. The usual case, that of decrease in conductivity in passing from the solid to the liquid state, is apparently due to a sudden increase in the number of positive centers. This is what one might expect since there is, apparently, a reduction in the forces of cohesion.

It seems probable that at low temperatures the molecules of a metal are gathered in clusters which act as single positive centers and that as the temperature is raised the increased activity of the molecules causes these clusters to break up slowly. The complete theory should, therefore, take account of the change in the cross-sections of the clusters as they break up as well as the change in their number. What the change in the cross-section is must depend upon the number and arrangement of the molecules in each cluster, and any general expression must represent a mean rate of change in the cross-sections. Since the number of positive centers must increase faster than their average cross-section decreases, the change in the former is more important than that in the latter.

In the theory as developed in this paper no allowance has been made for the expansion of the metal as the temperature is raised. The complete theory ought to take account of this expansion. The correction, however, is likely to be quite small.

It is obvious that an exhaustive study of the quantitative relations of this theory and experiment ought to be made. We have shown that qualitatively it is capable of explaining all of the phenomena considered if we exclude very low temperatures. It is also capable of explaining each of these phenomena separately quantitatively, but it remains to be seen to what extent the values of the constants involved are identical when different phenomena are compared. The writer is now carrying out the necessary computations to put the theory on a quantitative basis and hopes to publish the results of this work in the near future.

Physical Laboratory,
University of Oregon,
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