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side layer." The priority in postulating it belongs, however, to Prof. A. E. Kennelly whose paper on this subject appeared in March, 1902 (*Electrical World and Engineer*, p. 473). *Heaviside's* article was published in December, 1902 (*Encyclopaedia Brittannica*, Vol. 33, p. 215) and was written in June, 1902, according to his own testimony (*Electromagnetic Theory*, Vol. 3, p. 335).

<sup>2</sup> E. g., A. Sommerfeld und I. Runge, Ann. Physik, 35, p. 290, 1911.

\* E. g., M. v. Laue, Enzyklopädie Math. Wissenschaften, Vol. 5, p. 424, 1915.

<sup>4</sup> W. Wien, *ibid.*, p. 130.

<sup>5</sup> P. O. Pedersen, Proc. Inst. Radio Engineers, 17, p. 1750, 1929.

# RECENT PROGRESS IN THE DUAL THEORY OF METALLIC CONDUCTION

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In 1921 I published<sup>1</sup> a "Summary" of the numerical results tentatively arrived at by means of the dual theory of conduction, especially the values of the "characteristic constants" of the various metals dealt with. Recently I have revised these numerical estimates, availing myself of some new data furnished by the International Critical Tables and applying the results of more mature reflection upon the problem with which I am engaged. The present paper may be regarded as a revision of the "Summary" above referred to. It is not a complete statement of all the features and applications of the dual theory in its present state of development, but it undertakes to show what measure of success this theory has attained in dealing numerically with the relations between electrical conduction, thermal conduction, the Thomson effect and the Peltier effect, in eighteen metals, including two alloys.

The "characteristic constants" of a metal, according to this theory, are the z, q, C,  $C_1$ ,  $C_2$ ,  $\lambda'_c$  and s contained in the following equations:

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

$$(\kappa_f \div \kappa) = C + C_1 t + C_2 t^2 \qquad (2)$$

and

$$\lambda' = \lambda'_c + skT. \tag{3}$$

In (1) n is the number of free electrons contained in unit "free space" within a metal at temperature T. By "free space" is meant space in which the free electrons can move as gas particles—that is, the whole volume of the metal less that part from which the free electrons are excluded by the atoms and ions. How much the "free space" differs from the total volume I cannot at present undertake to say, but the distinction

here made, analogous to that which is familiar to all who have dealt with the van der Waals equation for an imperfect gas, seems to be a valid and necessary one.

In equation (2)  $\kappa_f$  means that part of the total specific electric conductivity,  $\kappa$ , which is due to the free electrons, the other part, which will be called  $\kappa_a$ , being due to the "associated" electrons which are supposed to progress through the metal by passing from an atom to an adjacent ion without becoming free, and so without sharing the energy of thermal agitation. The *t* indicates temperature above 0°C.

In equation (3)  $\lambda'$  means the amount of energy, in ergs, required to dissociate an atom within the metal, thus producing a free electron, with a full complement of thermal energy, and a positive ion, both products remaining within the solid metal. The k is the Boltzmann gas-constant.

It is quite possible that, in order to meet all the conditions of the case, some of these so-called "characteristic constants," the q and the s, for example, must be supposed to vary slightly with temperature, but provisionally, and for the range of temperature between 0°C. and 100°C., this being the whole range with which I am at present concerned, they are to be treated as constants.

These three equations, with the interpretations here put upon them, embody the fundamental assumptions on which the dual theory of conduction is based. Our immediate concern is to derive numerical values for each of the "characteristic constants," except z, for every one of the metals with which we here have to do.

To determine the values of six unknown quantities we need to have six independent equations connecting these quantities. Three of the needed equations I have obtained from a study of the Thomson effect. These three equations, which are too long to be reproduced here, were first derived in a paper published by myself in 1920 (*Proc. Nat. Acad. Sci.*, **6**, pp. 139–154, equations (14), (15), (17)) and were revised the same year (*Ibid.*, **6**, pp. 613 and 614).

The fourth equation to be used for our present purpose is the expression for thermal conductivity,  $\theta$ , in the terms of the dual theory. Such an expression is given as equation (20) in a paper<sup>2</sup> published in 1926, where its derivation also is given. But I now use a slightly different form, which is

$$\theta = \left(\frac{k}{\hat{e}}\right)^2 \kappa_f \left[\frac{\kappa_a}{\kappa} \left(s + q - 1.5\right) \left(\frac{\lambda'_e}{k} + sT\right) + 2T\right].$$
(4)

Here the only new letter is e, which indicates the electron charge, 1.59  $\times$  10<sup>-20</sup>, a quantity which is to be taken with the positive sign in all of my discussions of the dual theory. The new feature of this revised expression for  $\theta$  is the term 2*T*, introduced in order to take account of that part of thermal conduction which is due to the mere process of diffusion of the

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free electrons along a temperature gradient, as distinguished from their general tendency to drift down this gradient. The contribution thus made to  $\theta_i$ , which contribution I shall call  $\theta_i$ , is

$$\theta_l = \left(\frac{k}{e}\right)^2 \cdot \kappa_f \cdot 2T. \tag{5}$$

The subscript l refers to Lorentz, who, taking the whole of electrical conduction to be due to the free electrons, wrote<sup>3</sup> the equivalent of

$$\theta = \left(\frac{k}{e}\right)^2 \cdot \kappa \cdot 2T$$

It seems probable that, in order to get a complete expression for  $\theta$ , it would be necessary to add to the second member of equation (4) a term representing the contribution made by the agitation of the atoms in their lattice arrangement; but for the present I have undertaken to get on as well as I can without this, not knowing how great it should be. It is possible that the somewhat unsatisfactory character of the results, presently to be shown, which my calculations give for  $\theta$  at 100°C. is due to this omission.

The fifth equation to be used in evaluating the constants is derived from one which I published in 1921,<sup>4</sup> but the full significance of which I have only recently appreciated. This latter equation is equivalent to

$$\frac{n_{\alpha}}{n_{\beta}} = \exp \left[ (\lambda_{\beta}' - \lambda_{\alpha}') \div kT \right].$$
 (6)

Substituting for n and  $\lambda'$  in (6) by use of (1) and (3), then writing the equation in logarithmic form, differentiating with respect to T and finally multiplying by T, I get

$$q_{\alpha} - \frac{(\lambda_c')_{\alpha}}{kT} = q_{\beta} - \frac{(\lambda_c')_{\beta}}{kT}.$$
 (7)

Now in obtaining (7) q,  $\lambda'_c$  and s have all been treated as constants. But evidently, if q and  $\lambda'_c$  are strictly constant through any range of temperature,  $(\lambda'_c)_{\alpha}$  must equal  $(\lambda'_c)_{\beta}$  and  $q_{\alpha}$  must equal  $q_{\beta}$ . It is possible, however, by making  $(\lambda'_c \div k)$  small and making  $q_{\alpha}$  nearly, though not exactly, equal to  $q_{\beta}$ , to make equation (7) very nearly true and very useful for our present purpose.

What is the number which all the values of q should approximate? This question is not difficult to answer. In my previous (1921) estimation of the characteristic constants I had not discovered the restriction imposed by equation (7) and my values of q ranged from 1.2, for iron, to 1.6 for certain other metals. The mean, however, was not far from 1.5, a number which occurs repeatedly in the evaluating equations derived

from the Thomson effect and always in the combination (1.5-q). In fact, as a rule, an invariable rule for cases in which the Thomson effect is simply proportional to T, a metal having, according to my sign convention, a positive Thomson effect was found to have a value of q greater than 1.5, while a negative Thomson effect implied a value of q less than 1.5. This number, then, was plainly indicated as the one about which the values of q should cluster. Acting accordingly I have now found, as the smallest value for q, 1.49, in iron, and as the largest 1.505, in cobalt and in constantan. Meanwhile the value of  $(\lambda'_c \div kT)$  at 0°C. has fallen from a former maximum of 2.91, for bismuth, to a maximum of about 0.02, for magnesium. These changes have not only enabled me to comply with, or at least give respectful attention to, the condition suggested by equation (7); they have had a most happy result in my dealing with the numerical data of the Peltier effect.

The sixth and last of the equations needed for evaluating the constants is an expression, which I published in 1921,<sup>5</sup> for the Peltier effect between two metals  $\alpha$  and  $\beta$ . It is

$$\Pi_{\alpha\beta} = \begin{pmatrix} \kappa_{f} \\ \kappa \end{pmatrix}_{\beta} \lambda_{\beta} - \begin{pmatrix} \kappa_{f} \\ \kappa \end{pmatrix}_{\alpha} \lambda_{\alpha}.$$
(8)

 $\Pi_{\alpha\beta}$  means, with my convention as to algebraic signs, the amount of heat, in ergs, absorbed by the unit quantity of electricity,  $(10^{20} \div 1.59)$  electrons, in going from metal  $\alpha$  to metal  $\beta$ . I shall in all cases take bismuth as the metal  $\beta$ , because by so doing I have only positive values for  $\Pi_{\alpha\beta}$ . For my Peltier-effect numerical data, as for my Thomson-effect numerical data, I depend entirely upon the work of Bridgman as published<sup>6</sup> in his too-little celebrated paper on *Thermo-Electromotive Force, Peltier Heat and Thomson Heat under Pressure.* 

After the characteristic constants for bismuth have been found, so that the term  $((\kappa_f \div \kappa)\lambda)_{\beta}$  in equation (8) is known, I undertake to find for every other metal such a set of constants that this equation will give the observed value of  $\Pi_{\alpha\beta}$  at 0°C. But naturally the question arises how the constants for bismuth itself can be determined. Might we not vary the  $\alpha$  constants and vary those of  $\beta$  also in such a way that equation (8) would still give a value agreeing with the observed value of  $\Pi_{\alpha\beta}$  at 0°C.? Yes, but unless a particular set of constants is used for  $\beta$ , or bismuth, equation (8) will not give the correct, the observed, values of  $\Pi_{\alpha\beta}$  at both 0° and 100°C. This criterion, which I have arrived at almost accidentally after considerable experimentation, appears to be entirely satisfactory. After I had found a set of constants for bismuth and a set of constants for any other,  $\alpha$ , of my metals, which sets of constants complied with the other conditions imposed and, when used in equation (8), gave the observed values of  $\Pi_{\alpha\beta}$  at 0° and at 100°, I had no further trouble with the Peltier effect. Using the same set of bismuth constants and taking any other metal  $\alpha$ , I found that, when I had obtained for this metal a set of constants complying with the other conditions and satisfying equation (8) at 0°, the same set of constants satisfied equation (8) at 100°.

TABLE 1

VALUES OF THE "CHARACTERISTIC CONSTANTS"									
METAL	С	C1×10€	$C_2 \times 10$	• q	5	$\lambda_c' \div k$	ð0	δ100	$\tau \div T$
<b>A1</b>	0.1083	-0.47	7.33	1.499	4.75	2.8	0.11	0.15	-0.016 + 0.006t
Bi	0.338	-91.5	0	1.499	4.06	4.0	0.10	0.13	-3.2
Co	0.1545	197	0	1.505	<b>4.6</b> 0	2.6	0.11	0.15	7.8
Cu	0.0737	-17.4	0	1.499	6.45	<b>4.5</b>	0.15	0.21	-0.966
Gold	0.0686	-15.6	0.8	1.499	6.95	3.6	0.16	0.22	-0.934 + 0.001t
Iron	0.0380	24.1	35.2	1.490	8.49	3.4	0.20	0.27	1.78 + 0.0516t
Mg	0.0800	-0.15	0	1.4993	6.36	5.5	0.15	0.21	-0.008
Mo	0.0606	-68.8	11.9	1.495	7.31	3.3	0.17	0.24	-4.33 + 0.015t
Ni	0.1787	103.3	0	1.502	4.00	2.9	0.09	0.13	3.56
Pd	0.0934	66.7	0	1.503	6.12	3.4	0.14	0.20	3.52
Pt	0.0856	48.7	0	1.5025	6.36	3.7	0.15	0.21	2.67
Silv.	0.0727	-15.2	0	1.4995	6.60	2.5	0.16	0.21	-0.864
T1	0.0742	4.68	2.99	1.4995	6.60	3.2	0.16	0.21	0.268 + 0.0034t
Tin	0.0742	2.27	0	1.5001	6.85	3.2	0.16	0.22	0.134
Tung.	0.0578	-46.6	0	1.498	8.50	3.0	0.20	0.27	-3.41
Zn	0.0716	17.33	0	1.501	6.63	3.9	0.16	0.21	0.99
Con.	0.1423	143.7	0	1.505	6.41	3.6	0.15	0.21	7.94
Man.	0.0527	-10.2	-4.14	1.501	<b>9.4</b> 0	4.2	0.22	0.30	-0.828 - 0.0067t

In table 1 are assembled the values found for the "characteristic constants" of the eighteen metals, including the two alloys constantan and manganin, with which I have dealt.<sup>7</sup> The numbers for  $(\lambda'_c \div k)$  are here carried to one place only of decimals, though in some of my calculations I found it desirable to use two decimal places for this quantity. The  $\delta_0$  and  $\delta_{100}$  columns give approximately, in volts, the ionizing potentials within the several metals at 0°C. and at 100°C., respectively, these values being found from those of  $\lambda'$  in equation (3). The last column of the table gives, with my sign convention, the values of the Thomson effect, as found from the work of Bridgman above referred to. For each metal the value of  $\tau$  gives the amount of heat, in ergs, absorbed by the unit quantity of electricity,  $(10^{20} \div 1.59)$  electrons, in going from a place of temperature  $(T - \frac{1}{2})$  to a place of temperature  $(T + \frac{1}{2})$  within the metal. It is to be noted that, in all cases where  $\tau$  is a one-term quantity, q is greater than 1.50 when  $\tau$  is positive and less than 1.50 when  $\tau$  is negative.8

This last column of table 1 and columns 1, 2, 3, 5, 7 and 9 of table 2 contain the data which the dual theory of conduction endeavors to coordinate, through the "characteristic constants" of table 1 and the equations in which these constants are used. Unfortunately, the data which these columns give with respect to any one metal have in no instance all been derived from study of the same specimen of that metal. Thus I take all my thermoelectric data, as I have already said, from the work of Bridgman, but he did not measure specific conductivity, either electrical

TABLE 2

# Values at 0° and at 100 °C. of $\kappa$ , $\theta$ and II, in Absolute Measure

							(Π <sub>αβ</sub> )		$(\Pi_{\alpha\beta})_{100}$	
			θο >	< 10-5	θ100	× 10⁻⁵	X 1	0-4	×	10-4
METAL	K <sub>0</sub> × 10∙	κ <sub>100</sub> X 10•	OBS.	CALC.	OBS.	CALC.	OBS.	CALC.	OBS.	CALC.
Al	415	289	203	202	209	193	202.0	202.1	263.0	262.8
Bi	9.4	6.5	8.4	8.3	7.7	7.7	0	0	0	0
Co	110.6	81.0	<b>69.2</b>	<b>69</b> .0	69.2	76.3	155.9	155.9	172	171.3
Cu	643	<b>45</b> 0	388	<b>39</b> 0	381	365	210.8	211.2	279.6	280.0
Gold	450	322	296	294	296	282	211.1	211.1	279.8	279.3
Iron	112.4	69.3	61.9	61.7	59.8	59.7	247.3	247.4	309.7	309.5
Mg	242	$174 \cdot$	155	154.3	147	151.4	203.0	203.3	265.4	265.5
Mo	228	159	146	146.2	139.4	126.9	219.3	218.9	300.9	300.2
Ni	106	74.6	58.6	58.2	57.7	59.6	155.1	154.8	186.7	186.1
Pd	98.5	74.7	67.4	67.2	72.0	74.0	188.1	188.6	232.0	232.3
Pt	102.6	74.0	69.5	69.4	73.2	<b>72</b> .0	194.7	195.1	244.1	244.2
Silv.	668	475	419	417	412	398	210.2	210.4	278.3	278.2
T1	60.9	41.3	39	38.8	40.5	36.3	207.7	207.9	270.2	270.1
Tin	95.5	66	65.7	65.4	60.5	61.8	203.8	203.6	266.0	265.4
Tung.	194	147	1 <b>6</b> 0	159.2	158	152.2	207.5	207.8	284.3	284.4
Zn	181	127	113	112.5	111.3	110.3	211.5	211.7	273.3	273.0
Con.	<b>2</b> 0.4	20.4	<b>22</b> .0	21.9	29	32.5	108.3	108.4	106.4	105.9
Man.	22.7	22.7	20.8	20.8	26.4	27.7	206.9	206.6	275.1	274.3

or thermal, and so for much of my data I have had to depend on information given in the International Critical Tables, referring to the work of other men using different material, and in many cases the information thus obtained is very unsatisfactory for my purpose. Nevertheless, I have, in the procedure described in this paper for estimating the values of the constants, been obliged to treat the body of data which I have settled upon for any one metal as authoritative and self-consistent. Thus the values of  $\tau$  given in table 1 and those of  $\kappa_0$  and  $\kappa_{100}$  given in table 2 have gone into my calculations as absolutely true, and accordingly the values of the constants which have resulted from these calculations must The values of  $\theta$  and of  $\Pi$  given in columns be consistent with these data. 3, 5, 7, and 9 of table 2 have been used in a somewhat different manner. Instead of incorporating these values directly into my formulas, I have sought, by a tentative process, for a set of constants that would, when used in equations (4) and (8), respectively, yield values of  $\theta$  and  $\Pi$  agreeing satisfactorily with the so-called "observed" values of these quantities.

As regards  $\theta_0$ ,  $(\Pi_{\alpha\beta})_0$  and  $(\Pi_{\alpha\beta})_{100}$ , this undertaking has been entirely successful. In no case does the "calculated" value of one of these quan-

tities differ from the "observed" value by so much as one per cent, and even closer agreement could, I think, have been obtained by taking more pains in the selection of the characteristic constants. Anyone who is interested can with little trouble verify my "calculated" results for one or more metals by putting the needed constants, given in table 1, and the observed values of  $\kappa_0$  and  $\kappa_{100}$ , given in table 2, into equations (4) and (8), with due regard to equations (2) and (3).

The "calculated" values of  $\theta_{100}$ , on the other hand, do not agree very well with the "observed" values, as the latter are given in table 2. The mean of the calculated values is here about 2.8 per cent smaller than the mean of the "observed" values, and in individual cases the difference is much greater than this, about 10 per cent, for example, in the case of cobalt and molybdenum.

Is this partial failure sufficient reason for giving up the whole theory of conduction, in spite of its apparent success in other respects? I think not, though of course I am not an impartial judge in this matter. There are three possibilities which seem to me worth considering in this situation. First, it may be that my neglect, already acknowledged as unfortunate though for the present necessary, of the thermal conductivity due to agitation of the atoms is the cause of this defect regarding  $\theta_{100}$ . Second, perhaps a thoroughly successful dual theory of conduction will have to take account of a possible variation, with temperature, in the value of q or of s or of both. Third, perhaps more accurate data, obtained for each metal from the same specimen or from specimens of the same quality, would eliminate the difficulty now encountered. For example, in the case of cobalt, already mentioned as one of the metals for which the discrepancy regarding  $\theta_{100}$  is exceptionally large, I have put down 69.2  $\times$  10<sup>5</sup> as observed value of both  $\theta_0$  and  $\theta_{100}$ . But in fact all the information I have found in the I. C. T. concerning  $\theta$  in cobalt is that someone found the value to be  $69.2 \times 10^5$  at 30°C. in a specimen with 0.24% C, 1.4% Fe, 1.1% Ni, 0.14% Si. From this I have, by use of the Wiedemann-Franz rule,  $\theta \alpha \kappa T$ , found 69.2  $\times$  10<sup>5</sup> as the "observed" value of both 0° and 100°; for it so happens that in cobalt, according to the observations of Bridgman on the specimen he used, the value of  $\kappa$  is almost exactly inversely proportional to T. As to molybdenum, in which also the discrepancy between observed and calculated  $\theta_{100}$  is large, the I. C. T., volume 5, p. 218, give the value of the Wiedeman-Franz "constant" as 3.08 at 0° and 3.17 at  $100^{\circ}$ , the "theoretical" value for all metals being 2.23.

In fact, when I consider the many doubts attaching to the body of data with which I have dealt in this investigation, I am quite content to have an appreciable amount of discrepancy between the "observed" and the "calculated" values exhibited in columns 5 and 6 of table 2. Complete agreement between calculated and observed quantities everywhere would arouse, even in myself, a suspicion as to the soundness of my argument and the value of my results, for I should fear that I had somehow been reasoning in a circle and begging the questions at issue.

It is to be noted that my "observed"  $\theta_{100}$  values were not used at all in the determination of the "characteristic constants." Accordingly, if I had for every metal a body of data which I regarded as correct and selfconsistent, my theory, if sound and complete, should enable me to find by calculation the value of  $\theta_{100}$  for each metal independently of any use on my part of the observed value at the temperature in question. Thus the findings of the theory could be subjected to a genuine test. It seems possible, though I do not care to prophesy to that effect, that with full and satisfactory data concerning the electrical and thermal properties of metals the dual theory might account for those departures from the Wiedemann-Franz law which are so marked and at present so mysterious. I cannot help regretting that some fraction of the research energy and talent and material resources now devoted to attacks upon the constitution of the atoms cannot be turned to a study of the familiar but little understood properties of metals in their ordinary condition.

There is something more to be said concerning equation (6), the validity of which does not depend on the soundness of the dual theory of electric and thermal conduction as set forth by myself. Apparently this equation must be accepted by anyone who admits the existence of free electrons, with full thermal energy, within metals and admits also the conclusion, drawn from the observed equality of "stopping potentials" for photoelectrically emitted electrons, that the total energy of an associated, or valence, electron is the same in all metals in contact with each other at the same temperature. For with these conditions equation (6) is merely the Boltzmann law of equilibrium distribution of free electrons between the two joined metals,  $\alpha$  and  $\beta$ ,  $(\lambda'_{\beta} - \lambda'_{\alpha})$  being the amount of energy required to take an electron from the free state in  $\alpha$  to the free state in  $\beta$  by the following reversible process: association of a free electron in  $\alpha$ with an ion of  $\alpha$  to form a neutral atom, passage of the electron from the atom of  $\alpha$  into union with an ion of  $\beta$  at the junction of the metals, escape of the electron from this union into the free state in  $\beta$ .

What the dual theory, if correct, contributes here is the means of determining  $\lambda'_{\alpha}$  and  $\lambda'_{\beta}$  numerically and so finding the ratio  $(n_{\alpha} \div n_{\beta})$  in definite numerical terms for any two of the metals dealt with. It is true that equation (6) is primarily derived for metals in actual contact with each other, but is evident that no one of the quantities  $n_{\alpha}$ ,  $n_{\beta}$ ,  $\lambda'_{\alpha}$ ,  $\lambda'_{\beta}$ , occurring in this equation, can be dependent to any appreciable extent on the circumstance of contact or lack of contact between the metals. So equation (6), if it holds for two metals in contact, holds for the same two metals when separate, provided the two have the same temperature. From the values of s and  $(\lambda'_{c} \div k)$  given in table 1 we can, by use of equation (3), get the value of  $\lambda'$  for any one of our metals at any temperature from 0° to 100°C. Table 3 gives values of  $(n_{\alpha} \div n_{\beta})$ , at  $T = 273^{\circ}$  and at  $T = 373^{\circ}$ , for every metal dealt with,  $\beta$  being in every case

		14			•
	VALUES OF	$(n_{\alpha} \div n_{\beta}), \beta B$	eing in All Cases	TUNGSTEN	
METAL a	ат 0°С.	ат 100°с.	METAL $\alpha$	AT 0°C.	AT 100°C.
Aluminum	42.5	42.5	Nickel	89.1	89.1
Bismuth	84.7	84.7	Palladium	10.81	10.81
Cobalt	49.4	49.4	Platinum	8.49	8.49
Copper	7.69	7.76	Silver	6.68	6.68
Gold	4.71	4.71	Thallium	6.68	6.68
Iron	1.01	1.01	Tin	5.21	5.21
Magnesium	8.41	8.49	Tungsten	1	1
Molybdenum	8.93	8.93	Zine	6.4 <del>9</del>	6.49
Constantan	8.09	8.09	Manganin	0.40	0.41

tungsten. Tungsten is given prominence here because of the leading part it plays in studies of electronic emission and in other experiments bearing upon the value of n. According to the numbers given in this table the ratio  $(n_{\alpha} \div n_{\beta})$  is larger than 1 in every case except that of the alloy manganin. In the case of bismuth it is very large, 84.7, and in that of nickel still larger, 89.1. For copper the ratio given is about 7.7, and for constantan, composed of about 60% Cu and 40% Ni, it is about 8.1, a value lying between the ratios for nickel and copper, respectively, but much nearer the latter. For manganin, composed of about 84% Cu, 12% Mn and 4% Ni, the value of n appears to be especially small.

Of course, no great amount of confidence can be placed in values arrived at as these have been, but they seem to me worth recording, and it is possible that they may have some influence in suggesting the course of future experiments for direct evidence<sup>9</sup> as to the magnitude of n.

The experiments of Miss Colpitts<sup>10</sup> indicated, somewhat uncertainly,  $2 \times 10^{17}$  per cu. cm. of the metal as the lower limit of *n* in gold and  $9 \times 10^{15}$  per cu. cm. of the metal as the lower limit in tungsten. The ratio of these two *n*'s is about 22. The ratio given in table 3 for gold and tungsten, per cu. cm. of "free space" in each metal, is 4.7.

NOTE.—At the Solvay Conference of 1924, which dealt with the subject of electric conduction in metals, the question arose as to whether the Boltzmann distribution law in its simplest form holds between n, the number of "free" electrons, and  $n_0$ , the number of un-ionized atoms, per cu. cm. of the metal. Q being the amount of energy required to ionize an atom within the metal, the law in question can be stated, tentatively, thus:

$$n = n_0 \epsilon^{-\frac{Q}{kT}}.$$
 (A)

It was in fact so stated by O. W. Richardson in the following inquiry

(p. 128 of the *Conference Report*):<sup>11</sup> "Does the formula [given above] hold in the theory of quanta?"

A number of the conferees present confidently expressed the opinion that it did hold. Others, including Lorentz and Bridgman, expressed a doubt. A reader of the whole *Report* would be likely to get the impression that the Conference approved the use of the equation, in the form given above, as governing the amount of ionization within a metal. One member, speaking in support of this use, said, "The Boltzmann equation applies even in cases where one can apply the rules of quanta. It is thus that Einstein made use of it in 1917 in his derivation of the law of Planck."

The paper of Einstein here referred to is printed in the *Physikalische* Zeitschrift, vol. 18, pp. 121–128. The following passage occurs on p. 122: "According to the quantum theory a molecule of a given kind can, apart from its orientation and motion of translation, take only a discrete series of conditions  $Z_1, Z_2, \ldots, Z_n, \ldots$ , the internal energy of which shall be  $e_1, e_2 \ldots e_n \ldots$  If molecules of this sort belong to a gas of temperature T, the relative frequency  $W_n$  of the condition  $Z_n$  is given by the formula

$$W_n = p_n \ \epsilon^{-\frac{\epsilon_n}{kT}}, \qquad (5)$$

corresponding to the canonical distribution of states in statistical mechanics. In this formula  $k (= R \div N)$  is the familiar Boltzmann constant,  $p_n$  a number, independent of T, characteristic of the molecule and of its *n*th quantum condition, which can be defined as the 'statistical weight' of this condition. The formula (5) can be derived from the Boltzmann principle or by a purely thermodynamic method. Equation (5) is the expression for the widest generalization of the Maxwellian distribution law of velocities."

It is to be observed, however, that Einstein's eq. (5), when applied to the two quantum conditions m and n, gives

$$\frac{W_m}{W_n} = \frac{p_m}{p_n} \exp\left[-\frac{e_m - e_n}{kT}\right].$$
 (B)

There is nothing in Einstein's paper to show that  $(p_m \div p_n)$  must be 1. Accordingly it would seem that Richardson's question should be answered in the negative, unless the formula which he gave is to be amended so as to read

$$n = \frac{p_n}{p_{n_0}} n_0 \epsilon^{-\frac{Q}{kT}}, \qquad (C)$$

where  $(p_n \div p_m)$  is a factor to be determined.

- <sup>1</sup> Proc. Nat. Acad. Sci., 7, pp. 98-107(1921).
- <sup>2</sup> Physic. Rev., 28, pp. 392–417(1926).
- \* See p. 67 of his Theory of Electrons.

<sup>4</sup> Proc. Nat. Acad. Sci., 7, p. 63, eq. (8).

<sup>5</sup> Ibid., 7, p. 63, eq. 10.

<sup>6</sup> Proc. Amer. Acad. A. S., 53 (1918), pp. 269-386.

<sup>7</sup> I have not included cadmium in this list of metals. Bridgman studied cadmium as he did the eighteen other metals, but the value which he found for the Thomson effect in it is about ten times as great as that indicated by the observations of Fleming and Dewar (*Phil. Mag.*, 40, 5th series, 1895). Bridgman expresses the opinion that the specimen of cadmium which he studied may have been in an unstable condition, between two allotropic forms.

<sup>8</sup> Although I have arrived quite independently at the number 1.50 as the mean value of q in metals, I have already (*Nat. Acad. Sci. Proc.*, 15, p. 507) called attention to the fact that Richardson in deriving his  $T^2$  emission formula from the "classical kinetic theory" assumed the number of free electrons per cm.<sup>3</sup> of a metal to be proportional to  $T^{1.5}$ .

<sup>9</sup> I have discussed evidence bearing upon this magnitude in a recent paper, "On Electrons That Are 'Pulled Out' from Metals," *Proc. Nat. Acad. Sci.*, 15, 241–251 (1929).

<sup>10</sup> J. Frank. Inst., 206, Oct., 1928. <sup>11</sup> Gauthier-Villars, Paris, 1927.

# TWO CONTRADICTIONS IN CURRENT PHYSICAL THEORY AND THEIR RESOLUTION

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When Einstein examined the electro-magnetic theory of Lorentz at the beginning of this century, he found the principle of relativity for Galilean frames of reference, and the principle of the absolute velocity of light in vacuo, to be experimentally valid, yet contradictory. The necessity of rejecting the doctrine of absolute space and time for the principle of the relativity of simultaneity, in order to escape this contradiction, led him to the discovery of the special theory of relativity.

It is the purpose of this paper to show, by precisely the same type of argument, that this theory and the general theory which came out of it have given rise to two new contradictions in current physical theory which can be escaped only by introducing a radical but essentially simple amendment to the traditional atomic theory.

The Difficulty Concerning Atomicity and Motion.—The first contradiction will be demonstrated by establishing three propositions. (1) Atomicity is an inescapable fact. (2) Atomicity and the motion which it involves necessitate the existence of a referent in addition to the microscopic particles. (3) No such referent exists, according to current scientific theory.

1. Atomicity is an inescapable fact. The first argument for the atomic theory was given in Greek science by the pre-Socratic philosophers. They