THE TEMPERATURE COEFFICIENT OF CONTACT POTENTIAL.

By K. T. Compton.

FROM a consideration of the conditions of statistical equilibrium of the electrons inside and outside different metals in contact, Professor Richardson[1] has derived the equation

$$V_m - V_s = \frac{1}{e}(\phi_m - \phi_s) + P \tag{1}$$

for the contact difference of potential between the metals m and s. In this equation ϕ is the difference between the average potential energy of an electron inside and outside the metal. The latent heat of evaporation of an electron w which has been directly measured in several cases differs from ϕ only by the addition of a very small term denoting the difference between the rates of transfer of energy per electron by currents inside and outside the metal, if such a difference exists. This quantity, introduced, by Professor Richardson, appears to define one of the most important characteristics of the metal, since it is the measure of the work required to extract an electron from the metal. w has been measured directly[2] for platinum, osmium and tungsten and calculated for a large number of metals from data of thermionic[3] and photoelectric[4] emission.

The last term P which represents the Peltier difference of potential between the metals is comparatively very small. Neglecting this term, equation (1) is supported by such evidence as we have on the subject. A direct experimental test of the complete equation appears impossible owing to the extreme smallness of P in comparison with the limits of accuracy attainable in measurements of w. Equation (1) may, however, be transformed[5] to involve only the first and last terms, giving the equation

$$\frac{\partial}{\partial T}(V_m - V_s) = \frac{P}{T}, \tag{2}$$

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[1] "Electron Theory of Matter," pp. 455, 456.

[2] O. W. Richardson and H. L. Cooke, Phil. Mag., 20, p. 173, 1910; 21, p. 404, 1911; 25, p. 624, 1913; 26, p. 472, 1913; H. A. Wilson, Phil. Trans., A, 202, p. 243, 1903.

[3] O. W. Richardson, Phil. Trans., A, 201, p. 497, 1903.

[4] O. W. Richardson and K. T. Compton, Phil. Mag., 24, p. 575, 1912.

[5] "Electron Theory of Matter," p. 459 (37).

which should be capable of experimental test.[1] The object of this paper is to discuss the results of attempts to test this equation.

According to equation (2) we should expect the temperature coefficient of contact difference of potential to be very small. For iron and bismuth and iron and nickel, for instance, equation (2) leads to the values, at 50° C.,

$$\frac{\partial}{\partial T}(V_{\text{Fe}} - V_{\text{Bi}}) = 0.0000887 \text{ volt per degree,}$$

$$\frac{\partial}{\partial T}(V_{\text{Fe}} - V_{\text{Ni}}) = 0.0000324 \text{ volt per degree.}$$

For none of the common metals are the thermoelectric powers larger than these. Thus on changing the temperature from 0° C. to 100° C. we should expect to observe variations in the contact differences of potential of approximately 0.00887 and 0.00324 volt respectively, which are large enough to measure with suitable apparatus.

We have both direct and indirect experimental evidence on which to base a test of the theory. From certain photoelectric[2] and thermionic[3] experiments we may conclude that the temperature coefficient of contact difference of potential is less than the influence of disturbing factors and experimental error. But as the magnitude of these uncertainties considerably exceeds that of the effect under consideration we can obtain no positive information from this source.

Such direct experiments as have heretofore been made lead to values of the temperature coefficient which are entirely too large to be consistent with equation (2). Probably the most reliable results have been obtained by Erskine-Murray[4] and Burbridge,[5] who found temperature coefficients of contact potential varying between −0.0022 and 0.0043 volt per degree for different metals. These results are of the order of a hundred times too large to fit equation (2) and the measured values bear no obvious relation to the thermoelectric powers. Accurate measurements are difficult to make owing to the smallness of the effect in com-

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[1] It is perhaps worth while to call attention to the recent criticism of the reasoning employed by Professor Richardson by W. Schottky, Verh. d. D. Phys. Ges., 17, p. 109, 1915. This criticism is based largely on the results obtained by Schottky when he applies the energy principle to a thermodynamic cycle similar to that treated by Richardson and obtains an equation inconsistent with the corresponding one derived by Richardson. Schottky, however, seems to have misapplied the energy principle when he places the total heat absorbed equal to zero in the reversible cycle which is not isothermal (Equation (6), p. 113). When this is corrected his results are not inconsistent with those given by Richardson.

[2] R. A. Millikan and G. Winchester, Phil. Mag., 14, p. 188, 1907.

[3] W. Schottky, Ann. d. Physik, 44, p. 1011, 1914.

[4] Phil. Mag., 45, p. 424, 1898.

[5] Phys. Rev., 2, p. 183, 1913.

parison with superposed effects due to insulation charges, time changes and oxidization. Yet there seems to be no doubt but that the experimental results are not in accord with the theory, assuming the usual interpretation of these results to be correct.

Apparatus.—The experimental measurements thus far made have been by some form or modification of the variable condenser method. It seemed worth while to make measurements by the ionization method, in which the air between two plates is ionized by γ rays and the potentials of the plates so adjusted by a potentiometer that no current passes between them, the applied difference of potential being then equal to the contact difference of potential. As compared with the older method, this method has the advantages of greater accuracy, elimination of static charges developed by moving parts and quickness and convenience in manipulation.

A cross section of the apparatus and a diagram of the connections are shown in Fig. 1. *NN* and *FF* are the opposing nickel and iron faces, respectively, of two hollow metal boxes, each about $6 \times 4 \times \frac{1}{2}$ inch. These boxes are surrounded by hard rubber insulation *I* and fit in the cavity of the lead block *LL*. A tube of radium was placed at *R* so that the γ rays passing up through the fan-shaped groove *G* ionized the air between the plates *NN* and *FF*. Two tubes passing into each box served as intake and overflow for the stream of water which was used to regulate the temperature of the plates. This device, while clumsy, was preferable to heating in an oven because it permitted very rapid variations in the temperature. One box was connected to the potentiometer and subdivided millivoltmeter and the other to one pair of quadrants of an electrometer. The sensitiveness of the apparatus was such that the contact difference of potential could be measured accurately to the ten thousandth of a volt.

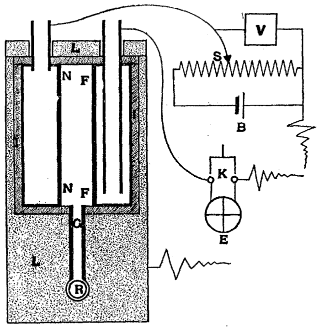

Fig. 1.

Time Changes.—It was first planned to polish the plates (with emery paper, then glass paper, then clean cotton), place them in position immediately and measure the contact difference of potential at different temperatures within a few minutes after polishing. When this was attempted, however, the measurements were very erratic and bore no resemblance to the true contact difference of potential. This effect did not disappear until four or five hours had elapsed after polishing and reappeared whenever the apparatus was slightly jarred or disturbed. Various tests made it evident that frictional charges, probably on the rubber insulation, were responsible for this spurious effect. Inability to avoid them when putting the boxes in place or polishing them in position made it necessary to wait several hours after polishing before making the desired measurements. During this interval as well as later the value of the contact difference of potential changed with time, the iron becoming more electronegative as is shown by Fig. 2. The solid curve is a true logarithmic curve whose equation is

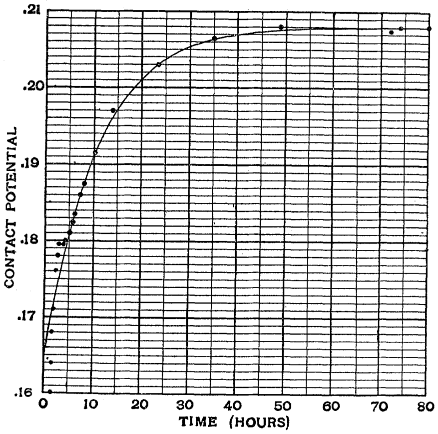

Fig. 2.

$$V_\infty - V = (V_\infty - V_0)e^{-kt} = (0.2080 - 0.1646)e^{-0.0925t} \qquad (3)$$

The experimental readings beyond five hours from the time of polishing fall almost exactly on the curve. The extreme regularity of the curve proves an accuracy of the experimental arrangement beyond anything hitherto attained in such measurements. Other similar tests yielded curves with the same values (approximately) of V_∞ and k but the values of V_0 varied somewhat.

The significant feature of these results is the fact that the iron became continually more electronegative with respect to nickel. This was probably due to oxidation of the iron—an explanation supported by equation (3) which is of the form typical of chemical reactions of this kind. This oxide film, however, must have been extremely thin since the surface of the iron appeared as brightly polished at the end as at the beginning of the test.

The Temperature Coefficient of Contact Difference of Potential.—In view of these results the effect of temperature was tried only after the initial erratic variations had subsided and usually after the lapse of an interval of about twenty-four hours from the time of polishing. In various tests the temperature was varied within the interval 20° C. to 60° C. with the following results:

0.00216 volt per degree.
0.00154
0.00166
0.00113
0.00177

Mean = 0.00165 volt per degree.

While the large variations in these results indicate the effect of some disturbing factor, their general indication is plain. They are in good accord with the results obtained by the other method and are about fifty times as large as the theoretical coefficient deduced from equation (2).

Discussion.—There are two alternatives in interpreting the bearing of these results. Either equation (2) and therefore equation (1) does not conform to the facts or else what is actually measured is not the real contact difference of potential between the metals. Various lines of evidence support this second alternative. The rapid formation of an oxide film, very thin yet sufficient to alter the normal contact difference of potential, has occurred during the progress of all experiments of this sort. Thus we actually measure the contact difference of potential between opposing oxide surfaces (possibly so thin that the effects of metal and oxide superpose), so that we should expect to find temperature coefficients equal to or largely affected by the thermoelectric powers of the oxides. It has been recently shown by Bidwell[1] that the metallic oxides in general possess extremely high thermoelectric powers, some of them being sufficiently large to account for the observed values of the temperature coefficient of contact difference of potential by the theory expressed by equations (1) and (2).

It is possible that surface layers of a gaseous nature contribute to increase the variation of surface potential with temperature. If this were a predominating factor, however, we might expect a "lag" in

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[1] Phys. Rev., 3, p. 204, 1914.

the potential change as the temperature is varied. No certain indication of such a lag was detected in these experiments.

Recently Professor Richardson[1] has shown that the presence on metals of surface films with large thermoelectric powers would account for certain peculiarities in the thermionic emission from metals.

Thus the status of the problem appears to be that no certain test of equation (2) has yet been made. The suggested explanation of the experimental results is certainly true to some extent but whether or not the entire discrepancy between theory and experiment may be thus accounted for is a question which at present cannot be answered. Preparation of surfaces and measurements in extremely high vacua, as were carried on successfully by Hennings[2] and Kadesch[3] can alone lead to a reliable test of the validity of equation (2).

The measurements described above were made in the physical laboratory of Reed College with the assistance of Mr. Ellis Jones of the senior class. I take pleasure in thanking him for his aid and for valuable suggestions.

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[1] Roy. Soc. Proc., A, 91, p. 524, 1915.

[2] PHYS. REV., 4, p. 228, 1914.

[3] PHYS. REV., 3, p. 367, 1914.