The Thermionic Work Function and the Slope and Intercept of Richardson Plots

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This article is a critical correlation of the slope and intercept of experimental Richardson lines with the quantities appearing in *theoretical* equations based on thermodynamic and statistical reasoning. The equation for *experimental* Richardson lines is $\log i-2\log T=\log A-b/2.3T$; A and b are constants characteristic of the surface, i is the electron emission current in amp./cm^2, T is the temperature in degrees K, $\log A$ is the intercept and $-b/2.3$ is the slope of experimental lines. Statistical *theory* based on the Fermi-Dirac distribution of electron velocities in the metal shows that i should be given by $\log i-2\log T=\log U(1-r)-w/2.3T$, where U is a universal constant which has the value 120 amp./cm^2 °K^2, r is the reflection coefficient, and w is the *work function.* A correlation of the experimental and theoretical equations shows that $b=w-Tdw/dT$, and $\log A=\log U(1-r)-(1/2.3)dw/dT$. Only when r is 0 and the work function is independent of the temperature, is it correct to say that the slope is $-w/2.3$ and that the intercept has the universal value $\log U$. But even when w is a function of T, it follows from a thermodynamic argument that the slope is given by $-h/2.3$, where the heat function h is defined by $h=(L_p/R)-(5/2)T$, L_p is the heat of vaporization per mol at constant pressure. The heat function is related to the work function by the equation $h=w-Tdw/dT$.

From experimental and theoretical arguments it is deduced that the reflection coefficient is probably negligibly small. Hence we conclude that *for most surfaces the work function varies with temperature,* since the intercepts of Richardson lines are rarely equal to log 120. This conclusion is to be expected since on Sommerfeld's theory, w depends on the number of free electrons or atoms per cm^3, which in turn varies with temperature due to thermal expansion.

The photoelectric work function should equal the thermionic work function but should not in general be equal to -2.3 times the slope of the Richardson line. The Volta potential between two surfaces having work functions w_1 and w_2 should equal $(w_1-w_2)k/e$ rather than $2.3k/e$ times the difference between the slopes of the Richardson lines for the two surfaces. The data from photoelectric and Volta potential measurements support the conclusion that the work function depends on temperature.

It is a well-established experimental fact that the thermionic emission current from nearly all surfaces can be represented by an equation proposed by Richardson[1] of the form

$$i=AT^2\epsilon^{-b/T}, \tag{1}$$

in which T is the temperature and A and b are constants characteristic of the surface. If $\log i-2\log T$ is plotted as a function of $1/T$, a straight line usually results. We shall call such a line a Richardson line. It is apparent that the slope of such a Richardson line is $-b/2.3$, while the intercept is $\log A$.

Considerable confusion has arisen, in the field of thermionic emission, in regard to the correlation of experimentally determined Richardson lines and theoretical equations based either on thermodynamic reasoning or on statistical reasoning. Thus the term "work function" has been indiscriminately used to designate any one of three distinct quantities: The slope of a Richardson line, the heat function h, and the work function w. h and w will be defined below. If the work function is independent of temperature, these three quantities have the same value; but if the work function varies with temperature it then becomes important to distinguish carefully between them. Considerable confusion has also arisen in regard to the interpretation to be placed on the intercept of the Richardson line. In particular, it is quite commonly felt that all Richardson lines should have the same intercept and that this point should be related to a universal constant whose value, as given by recent statistical theory, is 120 amperes per cm^2 per °K^2. This expectation is well founded only so long as the work function is independent of temperature. If the work function depends on tempera-

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[1] Richardson, *The Emission of Electricity from Hot Bodies*, 2nd Ed., Longmans, Green and Company, 1921.

ture, the intercept of a Richardson line should not correspond to the universal constant and should, furthermore, vary from one surface to the next.

It is the object of this paper to review carefully and critically how the slope and intercept of a Richardson line are related to certain quantities which appear in theoretical equations based on thermodynamic or on statistical reasoning. In doing this we will attempt to treat the problem quite generally, and will consider the case for which the work function varies with temperature. The work function will be correlated with the photoelectric work function and with contact potential.

THE THERMODYNAMIC EQUATION

From the Clausius-Clapeyron equation, which follows necessarily from the first and second laws of thermodynamics, and from the postulate that the electron vapor behaves like a perfect gas, it is shown in the Appendix that

$$\log i-2\log T=\log H+\log(1-r)-h/2.3T|_{T'}+(1/2.3)\int_{T'}^{T}(h/T^2)dT, \quad (2)$$

where T' is a fixed temperature in the experimental temperature range, H is a constant for a particular surface; it is independent of T but does depend on T' (see Appendix), r is the reflection coefficient, i.e., the ratio of the number of electrons reflected at the surface to the total number reaching it, only those electrons being considered that have velocity components normal to the surface sufficient to permit them to escape. Also

$$h=(L_p/R)-(5/2)T = \text{heat function expressed in °K} \quad (3)$$

where L_p = heat of vaporization of electrons per g·mol at constant pressure. As far as thermodynamics goes, h may vary with T and both H and h may vary with the nature of the surface.

In order to correlate Eq. (2) with the Richardson line we differentiate (2) with respect to $1/T$. If $\log i-2\log T$ is replaced by y,

$$\frac{dy}{d(1/T)}=-T^2\frac{dy}{dT}=-T^2\left(\frac{d\log(1-r)}{dT}+\frac{h}{2.3T^2}\right)$$
$$=-T^2\frac{d\log(1-r)}{dT}-\frac{h}{2.3}=-\frac{h}{2.3}. \quad (4)$$

The last step is strictly true only if $dr/dT=0$. The probable values of r will be considered later. From this consideration, it is probable that dr/dT is very small so that $-T^2d\log(1-r)/dT$ is negligibly small compared to $-h/2.3$. Subject to this consideration, it follows from Eq. (4) that *the slope of the tangent to an experimental Richardson line is always $-h/2.3$* no matter how h varies with T.

Two cases now arise: Either h is independent of T, or h is a function of T in the experimental temperature range. In the more general case, the Richardson line must be a curved line whose slope at any value of $1/T$ is equal to the value of $-h/2.3$ for that temperature. Naturally, we cannot represent such a curved line by the empirical Eq. (1). However, at any temperature T_1 in the experimental range, we can draw a tangent to the curve. The equation of this tangent can be represented by Eq. (1) if $\log A$ is the intercept and $-b/2.3$ the slope of the tangent. Hence it follows that the equation of the tangent at $T=T_1$ is given by

$$y=\log i-2\log T=-b/2.3T+\log A,$$

where $b=(h)_{T_1}$ and

$$\log A=\log H+\log(1-r)-h/2.3T|_{T'}+h/2.3T|_{T_1}+(1/2.3)\int_{T'}^{T_1}(h/T^2)dT. \quad (5)$$

If T_1 is taken at T', it is seen that $\log H(1-r)$ is the intercept of the tangent at T'.

Since empirically Richardson lines are straight lines, it follows that h is independent of T in the experimental range. Since h is simply related to L_p, the heat of vaporization by Eq. (3), we propose to call h the "heat function" to distinguish it from the "work function," to be defined later. If h is independent of T, Eq. (5) reduces to

$$\log A=\log H(1-r). \quad (5a)$$

While $\log A$ is a constant characteristic for any particular surface, there is nothing in the derivation that implies that log A or the intercept of the Richardson line, should be the same for all surfaces.

THE STATISTICAL EQUATION

Theoretical emission formulae have been derived by means of statistical reasoning. On the basis of Sommerfeld's[2] application of the Fermi-Dirac statistics to metals, Nordheim[3] has shown that i should be given by

$$i = U(1-r)T^2\epsilon^{-w/T} \tag{6}$$

or

$$\log i - 2\log T = \log U(1-r) - w/2.3T, \tag{6a}$$

where U is a universal constant given by $U = 4\pi mk^2e/h^3 = 120$ amp./cm^2/°K^2; k is Boltzmann's constant; h is Planck's constant; e is the electronic charge; r is the reflection coefficient previously defined. The quantity w, which appears in Eq. (6), we will call the "work function." It is apparent that the units in which w must be expressed in Eq. (6) are those of temperature in °K. The work function expressed in ergs, which we will call W, is equal to kw, where k is Boltzmann's constant. φ the work function in equivalent volts, is equal to wk/e or $w/11{,}606$.

W is defined as $W_a - W_i$. W_a is the difference in potential energy between an electron inside and outside the metal or the work an electron must do against electrical and other forces while it escapes from the surface. W_a depends on the nature of the metal, the nature of the surface and, in general, may depend on the temperature. W_i appears as an integration constant in equations dealing with the Fermi distribution; to a high degree of approximation[4] its value is given by the equation

$$W_i = kw_i = (h^2/2m)[3nv'/4\pi G]^{2/3}, \tag{7}$$

in which h = Planck's constant; m = mass of electron; n = number of atoms per cm^3; v' = number of free electrons per atom, usually assumed to be equal to the number of electrons in the outermost shell; G is the statistical weight and is equal to 2 for electrons. Since W_i depends on n, which varies with T, W_i depends on the temperature. Hence the work function w, in general, depends on the metal, its surface, and its temperature.

There are three interesting possibilities in Eq. (6): $dw/dT = 0$, a constant other than zero, or a function of T.

(1) If $dw/dT = 0$, i.e., if w is a constant independent of T, then the Richardson plot should yield a straight line whose slope is $-w/2.3$ and whose intercept is log $U(1-r)$ or log 120 $(1-r)$. This means that all surfaces for which $dw/dT = 0$ will have the same intercept corresponding to the log of the universal constant U, provided $r = 0$, so that

$$b = w \tag{8}$$

and

$$\log A = \log U. \tag{8a}$$

(2) If $dw/dT = \alpha$, where α is a constant $\neq 0$, then $w = w_0 + \alpha T$. w_0 is an integration constant: It is the value the work function would have at absolute zero provided the relation between w and T held for all temperatures down to absolute zero. Since we cannot test this assumption at low temperatures and since this proviso is probably not true, we avoid such phrases as "work function at absolute zero" and consider w_0 merely as a characteristic constant. For the case we are considering the Richardson plot will still be a straight line whose slope is $-w_0/2.3$, and whose intercept is log $U(1-r) - \alpha/2.3$, so that

$$b = w - \alpha T = w_0 \quad \text{or} \quad w = w_0 + \alpha T \tag{9}$$

and

$$\log A = \log U(1-r) - \alpha/2.3 \tag{10}$$

or

$$\alpha = 2.3\,(\log 120(1-r) - \log A).$$

(3) Finally if dw/dT is a general function of T, the Richardson line will be a curved line; the tangent at any point corresponding to a temperature T will have a slope equal to $-1/2.3(w - Tdw/dT)$ and an intercept equal to log $U(1-r) - (1/2.3)dw/dT$; w and dw/dT being taken at

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[2] Sommerfeld, Zeits. f. Physik **47**, 1 (1928). An excellent review of Sommerfeld's theory is given by Darrow in Rev. Mod. Phys. **1**, 90 (1929).

[3] Nordheim, Zeits. f. Physik **46**, 833 (1928).

[4] The second term in the expansion for W_i is $-[2m(\pi k)^2/12h^2](3nv'/4\pi G)^{-\frac{2}{3}}T^2$. This term leads to a temperature coefficient of W_i that is of the order of 10^{-6} volt per degree at 1000°K. This coefficient can be neglected in comparison with the temperature coefficient due to variation of n with temperature; it is of the order of 10^{-4} volt per degree, as will be shown later.

temperature T, so that

$$b = w_T - T\,dw/dT|_T \tag{11}$$

and

$$\log A = \log U(1-r) - (1/2.3)dw/dT\,|_T. \tag{12}$$

The proof of these statements follows: In Eq. (6a) let $y = \log i - 2\log T$. Then the slope of the tangent to a Richardson curve is

$$\begin{aligned} -b/2.3 &= dy/d(1/T) \\ &= (-1/2.3)[w + (1/T)dw/d(1/T)] \\ &= (-1/2.3)(w - T\,dw/dT). \end{aligned} \tag{13}$$

The equation of the tangent at a point corresponding to a temperature T_1 will be $y = (-1/2.3)(w_1 - T_1 dw/dT|_1)1/T + \log A$ where $\log A$ represents the intercept. When $T = T_1$, y must have the value $\log U(1-r) - w_1/2.3T_1$ so that $(-1/2.3)w_1/T_1 + (1/2.3)dw/dT + \log A = \log U(1-r) - w_1/2.3T_1$ or

$$\log A\,|_{T=T_1} = \log U(1-r) - (1/2.3)\,(dw/dT)\,|_{T=T_1}. \tag{14}$$

The proof of cases 1 and 2 follow from Eqs. (13) and (14) if $(dw/dT) = 0$ or α, respectively.

By combining the expression for the slope in terms of the work function w (Eq. (13)) with that in terms of the heat function h (Eq. (4)) it is easily seen that $-h = -w + T dw/dT$ or

$$h = w - T dw/dT. \tag{15}$$

This equation, which gives the relation between the heat function and the work function, is of the same form[5] as that between the change in free energy F and the change in total energy E namely,

$$E = F - T(dF/dT). \tag{16}$$

In a similar way by combining the expressions for $\log A$ in the thermodynamic Eq. (5a) with that in the statistical Eq. (14), it follows that $\log U = \log H + (1/2.3)dw/dT|_{T'}$. This equation and Eq. (15) do not contain r or any of its derivatives. This might have resulted from the simplifying assumptions we made with regard to r. However, one can rigorously derive these two equations by a direct comparison of the theoretical equations, without making any assumptions regarding r.

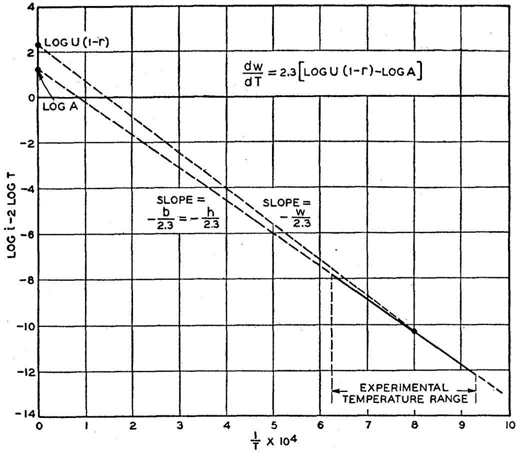

FIG. 1. Typical Richardson plot.

From Eq. (13) it is clear that the slope of a Richardson line is, in general, not equal to $-w/2.3$; it becomes equal to this quantity only if w is independent of the temperature. From Eq. (4) it is clear that the slope of a Richardson plot is always equal to $-h/2.3$. It is for this reason that we propose the term "heat function" for the quantity h and restrict the term "work function" for the quantity w.

These results can perhaps best be summarized by reference to a Richardson plot such as Fig. 1. The solid straight line represents the experimental data for a monomolecular layer of thorium on tungsten.[6] Its slope equals $-h/2.3$. Since the slope is constant, h does not vary with T. The intercept of the empirical line is $\log A$. If any point on the solid line is connected with a point on the y axis corresponding to $\log U(1-r)$ or $\log 120(1-r)$ by means of a dashed line, the slope of this line will be $-w/2.3$. w will depend on the particular point on the solid line; hence w will vary with T; if the empirical line is straight, w must vary linearly with T. dw/dT is given by 2.3 ($\log U(1-r) - \log A$).

From Eq. (14) it is clear that the intercept of a Richardson line is equal to the logarithm of the universal constant U, only if: (1) $r = 0$ and

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[5] Schottky pointed out this relation in Phys. Zeits. **20**, 49 (1919).

[6] Brattain and Becker, Phys. Rev. **43**, 428 (1933).

(2) $dw/dT=0$. It therefore becomes necessary to investigate the probable values of r and dw/dT or α more closely.

ON THE REFLECTION COEFFICIENT r

The reflection coefficient r for those electrons that come from within the metal and leave the surface has already been defined. One can also define a reflection coefficient r' for electrons impinging on the surface from outside of the metal. This coefficient is equal to the ratio of the number of electrons reflected to the total number incident. For a given surface these two coefficients r and r' should be equal. One reason for this is that equilibrium could not occur at such a surface unless r and r' were equal. Hence we can arrive at values of r by determining values for r'.

Values of r' will in general depend on the speed of the incident electrons. We are here concerned with electrons that have thermal speeds, or electrons that have on the average about 0.1 volt equivalent energy. Consider such an electron as it approaches a tungsten or molybdenum surface for which W_a is approximately 10 volts. When the electron gets within a few hundred atom diameters of the surface the surface forces will become appreciable, and the electron will be accelerated towards the surface. When it reaches the surface its total energy should correspond to $0.01+10.0$ or 10.1 equivalent volts. If by chance it now makes the right kind of collision, its velocity may be changed so that it then travels outward in a direction normal to the surface. If it has not lost energy in this process it may then escape and be counted as a reflected electron.

The angle that a 10.1 volt reflected electron must make with the normal to the surface in order to escape is quite small. Moreover, some of the energy of the incident electron may be dissipated. There are two possible mechanisms by which such energy dissipation may occur. As the electron moves with respect to the surface, it induces motion in the charges on the surface and these charges must suffer I^2R losses. This energy loss must come from the incident electron. The incident electron, while it is in the metal, has a velocity that is greater than the average velocity of the electrons in the metal and therefore has a chance of losing some of its energy in encounters with these electrons. Compton and Langmuir[7] have made a calculation on the magnitude of these two sources of energy dissipation and they conclude that only an extremely small fraction of incident electrons would lose less than 4 percent of their energy. Since a 10.1 volt electron would only need to lose 1 percent of its energy to be trapped, we see that the number of reflected electrons should be very small for incident electrons starting with 0.1 volt equivalent energy.

From these considerations it should be expected that for low velocity incident electrons r' should be quite small and should probably approach zero for zero velocity. It should also be expected that as the velocity of the incident electrons was increased, the chance of escape would increase rapidly, and that for high enough incident velocity an electron would even have some chance of transferring enough energy to a metal electron in such a way that both electrons could escape. In other words, one would expect that at large enough incident velocities the secondary emission might even be greater than the incident current. These expectations are confirmed by all experiments on secondary emission[8] in a high vacuum. They are also confirmed by experiments on the reflection coefficients for electrons striking a clean molybdenum surface in a gaseous discharge.[9] Hence we conclude that for incident electrons having thermal energies, r' and r must be quite small.

Theoretical values of r can be computed from the wave-mechanical theory of the electron if the curve for the potential energy of the electron as a function of the distance from the emitting surface is known or is postulated. In particular the shape of this curve near its maximum and the height of the maximum are the only important factors for an approximate calculation. Dushman[10] reviews the method and gives the equa-

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[7] Compton and Langmuir, Rev. Mod. Phys. **2**, 123 (1930), especially 172 and 173.

[8] See e.g. data on W by Ahearn, Phys. Rev. **38**, 1858 (1931), Fig. 4, and data on Mo by Hyatt and Smith, Phys. Rev. **32**, 929 (1928), Fig. 3. For additional references see reference 7 footnote 130.

[9] Langmuir and Jones, Phys. Rev. **31**, 401 (1928), see Fig. 15.

[10] Dushman, Rev. Mod. Phys. **2**, 381 (1930), see page 466.

tions which are involved. Nordheim[11] first applied this method to a potential energy function deduced from the image law for the force on an electron near a metal surface. He obtained a value of r less than 0.07. That the image law for the force on an electron is essentially the correct one for thermionic and photoelectrons is shown by the work of Schottky,[12] Becker and Mueller,[13] and Lawrence and Linford.[14] This work shows that the image law holds quite accurately for distances of 10^{-7} to about 10^{-4} cm from clean surfaces, and for 10^{-7} to about 3×10^{-5} cm from a composite surface such as thorium on tungsten. At still larger distances the potential energy curve for composite surfaces deviates from the one deduced from the image law of force, but this deviation should only slightly modify the value of r calculated by Nordheim. The reason is that when this potential energy curve is combined with the potential due to an applied field, the resulting curve has a very broad maximum at a distance from the surface greater than the distances mentioned above. For such broad maxima at such relatively great distances from the surface, the calculated value of r does not depend to any great extent on the exact shape of the maximum. Hence the computed value for r based on experimentally determined potential energy curves for composite as well as clean surfaces, should be about 0.07. It also follows from this discussion that since the shape of the potential energy maximum does not depend markedly on temperature, the reflection coefficient r should be independent of temperature. Hence, the value of r should be nearer to zero than to one at any temperature.

Values of r nearer to one than to zero have been computed by Fowler.[15] He assumed that the potential energy curve had a very sharp peak within one or two atom diameters of the surface, and that this peak was the highest maximum in the curve. It appears, however, that such a peak cannot exist because it leads to other predictions that do not agree with experimental results. Experiment shows that for clean surfaces $\log i$ increases linearly with the square root of the applied field E_a and that $d(\log i)/d\sqrt{E_a}=4.39/2.3T$. This relation was derived by Schottky[12] on the basis of the image law. For composite surfaces and low applied fields experiment shows that $d\log i/d\sqrt{E_a}$ is *greater* than it is for clean surfaces; at higher fields the Schottky relation is found to hold. In contrast with these experimental results, the sharp peak theory predicts that $d\log i/d\sqrt{E_a}$ should be considerably *less* than the value given by Schottky's relation. Hence, the predicted rate of increase in $\log i$ with applied field is less than that observed for clean surfaces and still more so for composite surfaces and low fields. The theory also predicts values of r' nearly equal to one for incident electrons having thermal velocities, whereas the experiments on secondary emission show that for velocities approaching thermal velocities r' tends to approach a value much closer to zero than to one. For these reasons we are of the opinion that a sharp peak of the nature discussed above does not exist for surfaces used in thermionic experiments.

From all this we conclude that r rarely exceeds 0.10, and quite likely its value is less than 0.10. Values such as these are so small that it seems hopeless at present to detect their effect on the intercept of the Richardson plot since experimental values of A can be determined only to within 10 percent even in the most accurate experiments. It thus seems safe to neglect r in the theoretical equations.

THE TEMPERATURE DEPENDENCE OF THE WORK FUNCTION

Experiment shows that for most surfaces the intercept of a Richardson plot yields values of A which are not equal to U; for some surfaces $A > U$ while for others $A < U$. From Eq. (14) it is clear that if $A > U$, *dw/dT cannot be 0*, but must be a negative quantity. Since r can have values only between 0 and 1, values of A larger than U cannot be accounted for by the presence of r in this equation. Experimental values of A, which are smaller than U, could be accounted for by assuming that r has values between 0 and 1. However, from the preceding section it follows that probable values of r can account only for values of A between 120 and about 110 amp./cm^2

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[11] Nordheim, Proc. Roy. Soc. **A121**, 626 (1928).

[12] Schottky, Phys. Zeits. **15**, 872 (1914).

[13] Becker and Mueller, Phys. Rev. **31**, 431 (1928).

[14] Lawrence and Linford, Phys. Rev. **36**, 482 (1930).

[15] Fowler. Proc. Roy. Soc. **A122**, 36 (1929).

°K². For values of A less than this, it necessarily follows that dw/dT or α cannot be 0 but must have positive values. Table I shows a few values of $\alpha/11{,}606$ in volts/°K as a function of A in amp./cm² °K². These were computed from Eq. (10) for $r=0$. To appreciate how small these values of α are, one need only compute the change in work function for a 1000° temperature interval for surfaces such as tungsten, molybdenum, or tantalum, for which $A=60$. Thus $\Delta w=0.58\times10^{-4}\times1000\doteq0.06$ volt; so that even over a 1000° temperature range the work function increases only by about 1.5 percent. For thoriated tungsten, for which $A=5$, $\Delta w\doteq2.7\times10^{-4}$ volt per degree or 0.14 volt for 500°K.

TABLE I. *Values of* $\alpha/11{,}606$.

A amp./cm² °K²	10^{-2}	1	10	60	120	500	1000	10,000
(α volts/°K) $\times10^4$	8.08	4.12	2.14	0.58	0	−1.24	−1.84	−3.82

For composite surfaces such as Th on W, Cs on W, or O on W one would expect the work function to depend on T because W_a should depend on T. For such surfaces the potential energy difference across the surface is increased or decreased, depending upon whether the adsorbed particles are electronegative or electropositive with respect to the underlying surface. The amount of change in W_a depends upon the fraction of the particles ionized or the degree of polarization or electrostatic moment per adsorbed particle. It would appear quite probable that this quantity should depend on the temperature. Hence W_a and W should also depend on temperature.

Additional evidence that the work function does indeed vary with T in the direction and by amounts calculated from values of A can be obtained from a consideration of expansion coefficients. From the definition of W_i as given by Eq. (7), it follows that W_i must vary with T for any metal which expands or contracts with T. It is also instructive to compute numerical values of W_i and dW_i/dT. In Eq. (7), n represents the number of atoms per cubic centimeter, while v' probably represents the number of electrons in the outermost shell. For most metals other than the alkali metals, $v'=2$. Values of n can be obtained from data in the *International Critical Tables*. n will, of course, vary with temperature. For W, Ta, Mo, and Pt, we find on this basis $W_i=9.1$, 8.4, 9.3 and 9.5 volts, respectively; while for $\Delta W_i/\Delta T$ in the operating temperature range we find, respectively, values of -1.3, -1.5, -1.7, and -1.9×10^{-4} volts per degree. If we tentatively assume that $\Delta W_a/\Delta T=0$, then $\Delta W/\Delta T=-\Delta W_i/\Delta T$ and these values would yield values of A equal to 27, 21, 17 and 13, respectively. Except in the case of platinum, these values deviate in the right direction from the theoretical value of 120, but are smaller than the experimentally reported values of about 60. The experimentally reported value of 60 should be smaller because it is based on an apparent surface area, while the true surface area of a filament is greater than the apparent surface area due to etching and facet formation. This effect however should only reduce the observed value of A to about 40 or 45 instead of 17 to 27. We can account for the higher values of A if we assume that $\Delta W_a/\Delta T$ is not equal to zero but has the same sign as $\Delta W_i/\Delta T$ and a value somewhat smaller than $\Delta W_i/\Delta T$.

Herzfeld[16] first pointed out that one would expect both W_a and W_i to vary with temperature because of expansion. For W_i he computed a temperature coefficient just as we have done above; he computed values of W_a and dW_a/dT from an approximate method of calculation given by Bethe.[17] Bethe himself pointed out quite clearly that his method gave only approximate values of W_a since several idealizing assumptions had to be made in calculating W_a; hence one could hardly expect the calculations to give accurate values for a second order effect such as the temperature dependence of W_a. The case is somewhat different for W_i and dW_i/dT, since the formula for W_i has been successfully used to explain second order effects. In Herzfeld's computation it appears that the effect of dW_a/dT is always larger than the effect due to dW_i/dT, and the overall effect predicts values of A greater than 120 for all metals which expand as the temperature increases. This contradicts the facts for most clean metals. Because of the uncertainties in the theoretical computations for dW_a/dT, the best procedure would appear to be

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[16] Herzfeld, Phys. Rev. **35**, 248 (1930).

[17] Bethe, Ann. d. Physik **87**, 55 (1928).

the following: Compute dW_i/dT as above; deduce values for dW/dT from the thermionic data; then deduce values for dW_a/dT from the difference of these two quantities.

The conclusions regarding the temperature variation of the work function receive still more support from a consideration of the relationship between the thermionic work function, the photoelectric work function, and contact potential and the dependence of these quantities on temperature. Before giving this evidence, however, it will be desirable to examine critically the correlation between these various quantities.

Correlation Between Thermionic and Photoelectric Work Functions

Because of the close correspondence between thermionic and photoelectric phenomena, it is of considerable interest to determine whether the photoelectric work function corresponds to the thermionic heat function or to the thermionic work function. The recent work of Fowler[18] and others[14] has made our concepts more precise and has furnished methods for determining a photoelectric work function w_p from experimental data. This w_p is defined in the same way as the thermionic work function w or w_t was defined above, namely, $w_p = w_a - w_i$. Hence it is to be expected that experimentally determined values of w_p should agree with those of w_t for the same surface and at the same temperature. In the past it has been customary to expect that the photoelectric work function w_p should agree numerically with the value of b deduced from the slope of the Richardson line.[19] This will be true only in those cases in which w is not a function of T. If w is a function of T, w_p should still agree with w_t but not with b.

Since the photoelectric work function is equal to the thermionic work function, it too should depend on T. More particularly, if the linear variation of w with T is valid down to temperatures used in photoelectric experiments, the photoelectric work function should be given by Eq. (9) in which the constants are determined from thermionic data. It is at once apparent that the temperature variation of the photoelectric work function is greatest for those surfaces for which α is large, i.e., for those surfaces for which the intercept of the Richardson line differs greatly from the universal constant, log 120. Now composite surfaces in general show larger deviations from this universal constant than do clean surfaces. Unfortunately no data of the variation of the photoelectric work function with temperature are available for such surfaces so we must content ourselves with the available data on clean surfaces. From Fowler's work[18] it is clear that the long wave-length limit gives an accurate value of the work function only if the experiment is performed at absolute zero. At other temperatures the tail of the Fermi-Dirac electron velocity distribution in the metal must be taken into account in determining the photoelectric work function.

Fowler[20] has analyzed the photocurrent as a function of frequency for Ag, Au and Ta at one or more temperatures, and has obtained values of the photoelectric work function in volts at these temperatures. His results are given in the third column of Table II. The fourth column gives values of the thermionic work function in volts obtained by using Eqs. (9) and (10). In the case of Ta, the thermionic constants are taken from the data of Dushman, Rowe, Ewald and Kidner.[21] They found for the intercept of the Richardson line a value of log 60 and for the slope a value equivalent to 4.07 volts. From these data we can determine φ at any temperature from the equation

$$\varphi = \varphi_0 + (\alpha)(k/e)T = \varphi_0 + (2.3 \log 120/A)T/11{,}606 \qquad (17)$$

or

$$\varphi = 4.07 + (2.3 \log 120/60)T/11{,}606 = 4.07 + 0.60 \times 10^{-4}T.$$

In the case of Ag and Au there are no correspondingly good data for the thermionic emission. It is found, however, that most of the ordinary metals have a value of A of about 60. We have, therefore, assumed that Ag and Au have this value of A and have adjusted φ_0 so

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[18] Fowler, Phys. Rev. **38**, 45 (1931).

[19] See e.g., DuBridge, Phys. Rev. **29**, 451 (1927) and **31**, 236 (1928).

[20] Reference 18, see especially table on page 52.

[21] Dushman *et al.*, Phys. Rev. **25**, 338 (1925).

TABLE II. *Comparison of thermionic and photoelectric work functions.*

Substance	Temperature	Photoelectric φ-volts	Thermionic φ-volts	Reference
Ta	293	4.10	4.09	Fowler
	973	4.14	4.14	
Ag	296	4.71	4.71*	Fowler
	673	4.76	4.73	
	873	4.75	4.75	
Au	296	4.86	4.86*	Fowler
	733	4.92	4.89	
	1013	4.92	4.92	
Palladium	305	4.96	4.96*	DuBridge
	400	4.97	4.966	
	550	4.97	4.975	
	730	4.97	4.985	
	830	4.98	4.991	
	925	4.98	4.997	
	1008	4.96	5.002	
	1078	4.97	5.006	
Molybdenum	303	4.14	4.14	DuBridge and Roehr
	940	4.16	4.18	

* These values are adjusted to agree with the photoelectric φ.

that the thermionic φ agrees with the photoelectric φ at $T=296$. The values of φ at higher temperatures are then computed from Eq. (17).

For palladium the photoelectric data were taken by DuBridge.[22] DuBridge also determined thermionic data for the same surface on which he took photoelectric data. For the thermionic φ_0 he gives 4.99 ± 0.05 volts. For the value of the thermionic φ at 305°K we have taken 4.96 volts, a value which is within the experimental error given by DuBridge. For molybdenum the data are taken from DuBridge and Roehr.[23] They too obtained thermionic data for the same surface on which they obtained photoelectric data. φ_0 varied from 4.14 to 4.17 volts, while A was equal to 55 amp./cm^2 °K^2.

The agreement between the temperature variation of thermionic and the photoelectric work function is better than one could expect considering the small value of the temperature coefficient and the difficulties of measuring temperatures and work functions accurately.

Fowler[18] specifically states that the values of $\nu_0 = \varphi e/h$ should according to his theory be independent of the temperature. However, he offers no proof of this statement, which places an unnecessary restriction on his theory. Indeed his theory is still applicable if the work function varies with T. Probably what Fowler meant to emphasize was that work functions determined by his methods for clean metal came out to be very nearly independent of temperature. Previous to this time it was customary to determine values for the photoelectric work function by plotting the photocurrent per unit light intensity against the frequency and extrapolating these curves to get the intercept on the frequency axis. Such curves have shown a considerable temperature dependence for this intercept. Fowler wished to emphasize the fact that this intercept did not measure the work function and that therefore the work function did not have any such temperature dependence as was shown by these intercepts. To say, however, that because of his analysis it has been shown that the work function correctly measured, is independent of temperature is an over statement. This is borne out by the previous analysis given in this paper.

These same comments also apply to certain statements made by DuBridge. He has said, "It is evident that it is now meaningless to speak of the 'temperature variation of the photoelectric threshold' for the true threshold is not temperature dependent. . . ." He might better have said that his measurements show that the temperature coefficient of the threshold for palladium must be less than 1×10^{-4} volt per degree. We deduce a value of 0.6×10^{-4} volt per degree. In a footnote DuBridge has said, "Evidently abnormal values of A cannot be ascribed to a temperature coefficient of $\nu_0 \cdots$." Our analysis shows this statement to be in error.[24]

Sometimes W_i or its equivalent is defined as the energy corresponding to the highest energy level which is occupied by an electron at absolute zero. According to this definition, W_i would not be defined at any other temperature than absolute zero. We feel that it is best to define W_i the

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[22] DuBridge and Roehr, Phys. Rev. **39**, 99 (1932).

[23] DuBridge and Roehr, Phys. Rev. **42**, 52 (1932).

[24] We have discussed these points with DuBridge and he has been kind enough to permit us to say that he is now of the opinion that the values of the temperature coefficient which we deduce are not inconsistent with his data.

way Sommerfeld, who originally introduced this concept, defined it, namely, by means of Eq. (7). This definition clearly shows that in general W_i must depend on temperature, because n depends on the temperature as discussed above.

DuBridge[22] and his associates[25] devised two new and ingenious methods somewhat similar to Fowler's method for analyzing photoelectric data. From the application of these methods to photoelectric data they conclude that the work function is independent of temperature. We will agree that this is approximately true for clean metals; they, however, do not consider it as an approximation. As a consequence they use methods of analyses and arrive at conclusions which we believe are only approximately true. Our reasons are given in the next two paragraphs.

The first[22] new method is based on the variation of the saturation photocurrent due to light of a fixed intensity and frequency with the cathode temperature. An analysis of this method shows that, strictly speaking, it is not a valid method unless the work function is independent of temperature. If, however, the temperature dependence is only slight—and this is true for the data they analyze—the method yields a good approximation to an average value of the work function. The fact that this average value agrees with an average φ obtained by other methods is no proof that φ is independent of T.

In the second[25] method the photocurrent for light of fixed intensity and frequency is measured as the retarding potential is varied; the cathode temperature is kept constant during any one test but is varied from one test to the next. Now from any retarding potential method alone it is possible to deduce values of the work function of the anode, but not of the cathode. Only by combining this value with a determination of the contact potential can the work function of the cathode be determined. DuBridge and his associates corrected or compensated for contact potential. However, no detailed analysis of contact potential is given and it is not stated how accurately contact potentials could be determined. Only by accurately determining the contact potential at each cathode temperature could this method determine how the cathode work function varied with temperature.

Correlation Between Work Functions and Contact Potential

The contact or Volta potential between two surfaces is determined by their thermionic constants. Here too the question arises whether the contact potential is more simply related to the heat function or to the work function. On the basis of quantum mechanics it would appear that the Volta potential V is equal to the difference in the work functions for the two surfaces rather than the difference in the slopes of the Richardson plots for the two surfaces.[26] Hence

$$V_{12}=(w_1-w_2)k/e=\varphi_1-\varphi_2. \tag{18}$$

A simple proof of this equation follows. Consider two insulated metal surfaces M_1 and M_2 in an evacuated enclosure at a constant temperature. For simplicity let the surfaces be large and parallel. Let w_1 and w_2 represent the work functions and suppose $w_1>w_2$. The saturation thermionic currents for the two surfaces will then be $i_1=UT^2\epsilon^{-w_1/T}$ and $i_2=UT^2\epsilon^{-w_2/T}$. Since $w_1>w_2$, $i_2>i_1$. Let us suppose that initially there is no field between the two surfaces. Since i_2 is larger than i_1, more electrons will go to M_1 than to M_2 and M_1 will become negatively charged with respect to M_2. This process will continue until the field in the space between M_1 and M_2, produced by the negative charge on M_1, is just sufficient to prevent any net flow of current between M_1 and M_2. When this condition is reached, equilibrium will be established. If n_1 and n_2 represent the concentration of electrons just outside of M_1 and M_2, respectively, and V_{12} is the potential difference between M_1 and M_2 when equilibrium is established, then it follows from Boltzmann's law that $n_1/n_2=\epsilon^{-eV_{12}/kT}$. The currents i_1 and i_2 that cross a square cm of surface per second just outside of M_1 and M_2, respectively, are proportional to n_1 and n_2. Hence it follows that $i_1/i_2=\epsilon^{-eV_{12}/kT}$, or $UT^2\epsilon^{-w_1/T}=UT^2\epsilon^{-w_2/T}\epsilon^{-V_{12}e/kT}$ or $-w_1/T=-w_2/T-V_{12}e/kT$ or $V_{12}=(w_1-w_2)k/e=(w_1-w_2)/11{,}600=\varphi_1-\varphi_2$. A little consideration will show

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[25] DuBridge and Hergenrother, Phys. Rev. **44**, 861 (1933) and W. W. Roehr, Phys. Rev. **44**, 866 (1933).

[26] Eckart, Zeits. f. Physik 47, 38 (1928).

that this same equilibrium condition must be reached irrespective of the initial condition; also irrespective of the shape of the metal surfaces.

When equilibrium has been established the two metals can be joined by wires or brought into contact. When this is done, no net current can flow in the wire. If a current did flow, the charges on the surfaces would change and the potential difference would no longer be equal to V_{12}. Hence a continuous current would flow in a circuit containing no e.m.f., all of whose parts were at the same temperature, in violation of the laws of thermodynamics.

If the two surfaces are joined by a wire before equilibrium has been established, a transient current will flow through the wire. The direction and magnitude of this current will be such as to build up a charge on the surfaces of the metals which is just sufficient to establish the Volta potential V_{12} in the space between the metals.

V_{12} can also be expressed in terms of the b and A for the two surfaces.

$$V_{12}=(k/e)[b_1-b_2+2.3T\log A_2/A_1]. \quad (18a)$$

This relation follows quite simply from the relations already given.

From Eq. (18) it follows that if w_1 and w_2 are functions of temperature, V_{12} will also depend on T. Conversely, if in an experiment values of V_{12} are determined for various temperatures of the cathode, while the anode is kept at a constant temperature, the change in w_1 with temperature is numerically equal to the change in V_{12}; similarly, if the temperature of the anode is changed while the temperature of a cathode is kept constant, the change in w_2 due to the change in temperature can be deduced from the observed change in V_{12}.

In a paper presented to the American Physical Society in 1923, C. J. Davisson[27] of these Laboratories found, among other things, that the contact potential between the hot cathode and a cold nickel anode depended on the temperature of the cathode. The cathode was a thoriated tungsten wire activated to approximately $f=0.8^6$. For a filament temperature of 1120°K he found a contact potential $V=-1.26$ volts; while for $T=1580$°K, V was -1.06 volts. This shows that the work function of the cathode increased 0.2 volt in 460°K. Hence $\alpha k/e=0.2/460=4.3\times10^{-4}$ volt per °K. For a thoriated tungsten filament, for which $f=0.8$, experiment shows that the intercept of the Richardson plot corresponds to an A of about 5. This in turn yields a value of $\alpha k/e$ of 2.7×10^{-4} volt per degree. These two values of α have the same sign and are of the same order of magnitude. Hence we can conclude that the reported change in contact potential with temperature is in the same direction and has the magnitude which we would predict from the interpretation we have put on the intercept of the Richardson plot.

ACKNOWLEDGMENTS AND SUMMARY

The writers are fully aware that some of the subjects treated in this article have been discussed before. We refer particularly to the valuable contributions by Schottky,[28] Herzfeld,[16] Bridgman[29] and Dushman.[30] It has, however, seemed worth while to correlate once more experiment and theory in the light of the theoretical advances that have recently been made in the application of quantum mechanics to thermionics and photoelectricity by Sommerfeld,[2] Nordheim[3] and Fowler.[18]

This correlation leads to the following definite conclusions: (1) A distinction should be made between the heat function h and the work function w; they are related by the equation $h=w-Tdw/dT$ and are equal only when the work function is independent of temperature. (2) The reflection coefficient r is very likely negligibly small. (3) The slope of the Richardson line measures h and from the slope and intercept of the Richardson line dw/dT and w can be determined. (4) The photoelectric work function, given by Fowler's analysis, should be equal to w rather than h. (5) The Volta potential is equal to $(w_1-w_2)k/e$ rather than $(h_1-h_2)k/e$. (6) The consideration of the physical meaning of the quantities in terms of which the work function w

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[27] Davisson, Phys. Rev. **23**, 299 (1924) (Abstract).

[28] Schottky, Handb. d. Experimental Physik **13** (Part 2) Akademische Verlagsgesellschaft, Leipzig, 1928.

[29] Bridgman, Phys. Rev. **27**, 173 (1926); **31**, 90 (1928); and **31**, 862 (1928).

[30] Dushman, Phys. Rev. **21**, 623 (1923) and Rev. Mod. Phys. **2**, 381 (1930).

is defined leads to the expectation that w will vary with temperature. (7) This temperature dependence becomes still more probable when one considers the evidence from photoelectric and contact potential experiments. In making this correlation and arriving at these deductions, we have avoided, as far as possible, the use of special assumptions or the postulation of any special mechanisms.

APPENDIX

The Clausius-Clapeyron equation, which follows from the first and second laws of thermodynamics, can be written as

$$(1/p)(dp/dT)=L_p/RT^2 \tag{1}$$

if the electrons act like a perfect gas; where p represents the pressure of the electron gas in an enclosure surrounded by the surface in question at temperature T; L_p is the heat of vaporization per g·mol at constant pressure, while R is the gas constant. From Eq. (1) it follows that

$$d\log p/dT=(1/2.3)L_p/RT^2 \tag{2}$$

and

$$\int_{T'}^{T} d\log p=(1/2.3)\int_{T'}^{T}(L_p/RT^2)dT. \tag{3}$$

The lower limit is taken at T' rather than at 0°K, to avoid the necessity of discussing, in this paper, the value that L_p/RT^2 approaches as T approaches zero. The safest procedure is to limit one's self to temperatures in the experimental temperature range and to define T' as some particular temperature in this range. From Eq. (3) it follows that

$$\log p=(\log p)_{T'}+(1/2.3)\int_{T'}^{T}(L_p/RT^2)dT. \tag{4}$$

We now define h by the equation

$$h=(L_p/R)-(5/2)T. \tag{5}$$

In this equation $(3/2)RT$ corresponds to the kinetic energy of the electrons in the vapor phase, while an additional RT represents the work that must be done against the pressure p. From Eqs. (4) and (5) it follows that

$$\log p=(\log p)_{T'}-(5/2)\log T'+(5/2)\log T \\ +(1/2.3)\int_{T'}^{T}(h/T^2)dT. \tag{6}$$

To obtain an expression for the thermionic emission current i, it is necessary to use a relationship based on kinetic theory, which correlates the pressure p with N, the number of electrons crossing a surface of 1 sq. cm area in unit time; the temperature T; the mass of the electron m, the reflection coefficient r and Boltzmann's constant, k. This equation is

$$N=(1-r)p/(2\pi mkT)^{\frac{1}{2}}. \tag{7}$$

Hence converting both p and p' to i and i',

$$\log i/i'=\log[(1-r)/(1-r')]+2\log T/T' \\ +(1/2.3)\int_{T'}^{T}(h/T^2)dT \tag{8}$$

or

$$\log i-2\log T=\log H(1-r)-h/2.3T\big|_{T'} \\ +(1/2.3)\int_{T'}^{T}(h/T^2)dT, \tag{9}$$

where $\log H$ is defined to be equal to $\log i'-\log(1-r')-2\log T'+h/2.3T\big|_{T'}$. $\log H$ is defined in such a way that if h is independent of T in the range between T' and T, then H will be a constant independent of T' as well as T. Eq. (9) is the same as Eq. (2) in the text.