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Photoelectric and Thermionic Investigations of Thoriated Tungsten Surfaces

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Photoelectric and thermionic data were obtained over a wide range of temperatures for several activations of a thoriated tungsten filament. The temperature dependence of the thermionic and photoelectric work functions are quite different. It is shown that this is to be expected for a nonuniform surface. The measured current density in either case is $i=(1/A)\int_s i_s\,ds$, in which i_s is given by either the Richardson-Dushman or the Fowler-DuBridge equation and A is the total emitting area. On the basis of a simple patch theory the integrations are carried out and show that (1) the saturation electron emission is independent of the size of the patches; (2) the observed or characteristic thermionic and photoelectric work functions for composite surfaces are different at low temperatures and approach each other at high temperatures; (3) the maximum and minimum values of the work function for a given surface do not vary linearly with temperature.

INTRODUCTION

The well-known experimental fact that the coefficient A in Richardson's equation for thermionic emission is not a universal constant has presented a problem of both experimental and theoretical interest. Actually several lines of evidence indicate that the discrepancy between A and the theoretical constant

$$U=4\pi^2mk^2e/h^3=120 \text{ amp./cm}^2\text{/deg.}^2 \quad (1)$$

may be ascribed to a temperature coefficient of the work function.[1] That is, in the equation

$$i=UT^2e^{-w/T} \quad (2)$$

the work function w may be a function of both temperature and applied field. Because Richardson lines usually are straight, it is assumed that higher derivatives of w than the first with respect to temperature are vanishingly small, so that

$$w=w_0+\alpha t, \quad (3)$$

in which w_0 and α are constants characteristic of the emitting surface, and may also be functions of the applied field.[2] Experimental values of A are related to the corresponding values of α through the equation

$$\alpha=2.303(\log U-\log A). \quad (3')$$

It is of course desirable to check this relation through independent measurements of α by other methods.

D. B. Langmuir[3] measured the contact potential difference between a tungsten filament and a tantalum anode as a function of temperature. He attempted to fit his results with a straight line, the slope of which he made equal to the negative of the temperature coefficient of the work function found by Nottingham from thermionic data.[4] His results are questioned in a recent paper by Reimann.[4a]

A more direct method of obtaining the temperature coefficient of the work function is to determine w for several different temperatures by the application of Fowler's theory to photoelectric data. In this way Brattain and Becker[5] deduced a value for the coefficient of palladium from the data of DuBridge and Roehr.[6] It was recognized, however, that more accurate data were needed.

Linford,[7] Smith,[8] and Glover[9] have shown that Fowler's theory may be applied to the composite surface of thorium on tungsten. Since a rather large temperature variation of the work function was to be expected for such a surface, it seemed worth while to make a more detailed study of the photoelectric and thermionic properties of thoriated tungsten.

APPARATUS AND PROCEDURE

The experimental tube was constructed in accordance with the conventional design in which

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[1] Becker and Brattain, Phys. Rev. 45, 694 (1934).

[2] Rose, Phys. Rev. 49, 838 (1936).

[3] D. B. Langmuir, Phys. Rev. 49, 428 (1936).

[4] Nottingham, Phys. Rev. 49, 78 (1936); *a*, Reimann, Proc. Roy. Soc. 163, 499 (1937).

[5] Reference 1, page 702.

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

[7] Linford, Rev. Mod. Phys. 5, 34 (1933).

[8] Smith and DuBridge, Phys. Rev. 46, 339 (1934).

[9] Glover, Ph.D. dissertation, University of Rochester, Spring, 1935.

three nickel cylinders are placed end to end and coaxial with the filament. The two end ones were connected together and used as guard rings; the middle one was fastened to a separate insulated support and was connected to a tungsten side lead. A molybdenum spring held the filament taut.[10] Potential leads were welded to either end of the filament. Through a slit in the central cylinder, opposite a quartz window, the filament could be illuminated for the photoelectric measurements. An ionization gauge and getter filaments of Th-W wire were included in the assembly.

Bake-outs of the whole assembly up to 500°C were alternated with bombardment and furnacing of the cylinders over a period of two weeks. During this procedure all the filaments were properly aged and thoroughly outgassed. The tube was finally sealed off the vacuum system and further cleaned up with the getter filaments until a pressure much less than 10^{-7} mm Hg was obtained.[11]

In order to control accurately the temperature of the filament, a circuit was constructed, which allowed values of the current to be read and maintained to better than one part in a thousand.

For the accelerating potential several B batteries were kept in a well-shielded dry box. A type P wall galvanometer in series with approximately 100 megohms was used as a high resistance voltmeter to measure it. All the measurements reported here were made for 100 volts collecting potential ($\sim$2640 volts/cm). An error of one-half volt was not significant since the work function approaches a constant value for about 100 volts applied potential as indicated on the work function—voltage diagrams determined by Glover[9] and by Brattain and Becker.[12]

A DuBridge-Brown amplifier[13] and a Leeds and Northrup type R galvanometer were used for photoelectric and weak thermionic measurements. This system allowed emission currents from 10^{-15} to 10^{-6} amperes to be measured. A multimeter, also in the circuit, could be employed for even greater emissions.

In order to obtain the temperature of the central part of the filament, a temperature *versus* current curve was made. The filament was "long" down to a temperature of 760°K and, therefore, in the thermionic range no lead loss corrections were necessary.[14] For this region and, in fact, down to a temperature of 600°K the Langmuir-Jones,[15] Forsythe-Watson,[16] and Forsythe-Worthing[17] tables were used, and a satisfactory scale was established. Points on it were checked with a pyrometer and also with an auxiliary tube. For that part of the curve from room temperature to 600°K the tables and formulas of Langmuir and Taylor were used.[18] In this region the temperature depends to a large extent upon the bulb temperature which, in these experiments, was taken to be equal to room temperature. For this reason two curves were determined for room temperatures of 292° and 302°K, respectively; and for intermediate values of room temperature, the filament temperatures were obtained by interpolation between them. Actually, these calculations were extended to 700°K. Temperatures between 600° and 800°K were determined so that the high and low ends of the two curves joined smoothly and yielded reasonable values in this region.

For the photoelectric measurements, spectral lines from a Cooper-Hewitt Uviarc were resolved by a single Bausch and Lomb monochromator with quartz lenses to focus the individual lines on the filament. Slit widths of 0.05 mm were used. A special table was built upon which to mount the monochromator and arc, so that they could be properly adjusted. Effects of stray light were investigated and found to be negligible. The relative intensities of the arc lines were measured with a vacuum thermopile connected to a high sensitivity low resistance galvanometer.

After activating the filament, thermionic emission measurements were made for both increasing and decreasing temperatures over a range where the surface was not altered by further activation or dispersion. Then at a series of temperatures below the thermionic range photoelectric data

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[10] Blodgett and Langmuir, Rev. Sci. Inst. **5**, 321 (1934).

[11] Pressures less than 5×10^{-8} mm Hg were unmeasurable with the apparatus used.

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

[13] DuBridge and Brown, Rev. Sci. Inst. **4**, 532 (1932).

[14] Langmuir, MacLane and Blodgett, Phys. Rev. **35**, 478 (1930).

[15] Langmuir and Jones, G. E. Rev. **30**, 310, 354, 408 (1927).

[16] Forsythe and Watson, J. O. S. A. **24**, 114 (1934).

[17] Forsythe and Worthing, Astrophys. J. **61**, 126 (1925).

[18] Taylor and Langmuir, Phys. Rev. **50**, 68 (1936); J. O. S. A. **25**, 321 (1935).

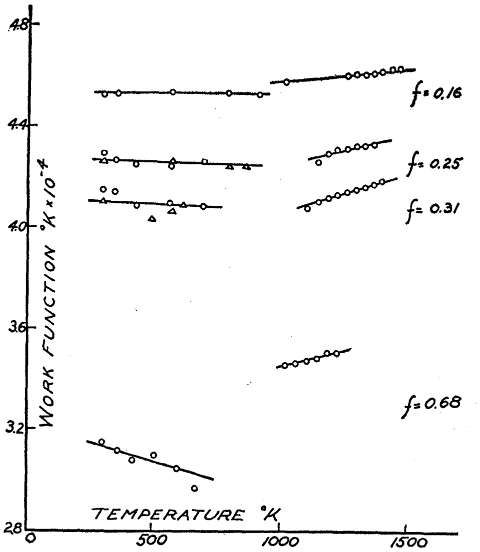

Fig. 1. Work function *versus* temperature curves for several activations of a thoriated tungsten surface, low temperature portions from photoelectric and high temperature portions from thermionic data. Small triangles represent data obtained on the following day of a regular run (represented by circles).

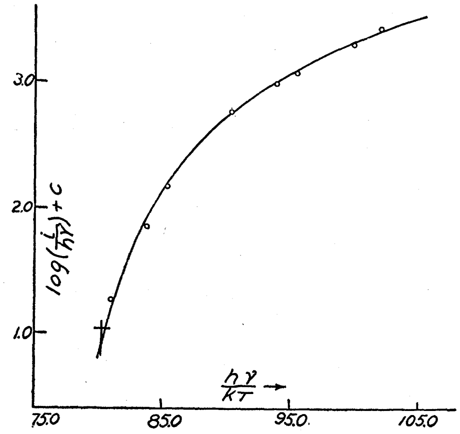

Fig. 2. Fowler plot of photoelectric data from a thoriated tungsten surface for which $f=0.16$ and $T=564.6°\text{K}$. The work function was found to be 45370°K.

were taken. Sufficient time was allowed between changes of temperature so that equilibrium conditions became established. At the end of a complete run the amplifier was calibrated. In this manner sufficient photoelectric data were secured so that Fowler plots could be made and work functions determined for a series of temperatures on surfaces of different activations.

Analysis and Interpretation of Data

The thermionic emission currents were first reduced to those for unit apparent surface. Then these values were introduced into the equation

$$w=2.303T\{\log U-\log i/T^2\}, \qquad (4)$$

in which log U was taken equal to 2.074. In this manner the *characteristic thermionic work functions* for a series of filament temperatures at various activations of the surface were determined. For any given activation these work functions are found to vary linearly with temperature with a *positive* increasing slope as seen in the right-hand group of line segments in Fig. 1.

The photoelectric emission currents, on the other hand, were plotted as log $(i/h\nu)$ against $h\nu/kT$ for each temperature and activation. A representative set of points fitted to a Fowler theoretical curve is shown in Fig. 2. The currents have been reduced to amperes per unit intensity of light. By an appropriate horizontal and vertical shift, the experimental points are brought into coincidence with the theoretical curve. Then the vertical shift corresponds to the absorption probability per quantum of light denoted by B; and the horizontal shift is just $h\nu_0/kT=w_p'/T$ in which w_p' is called the *characteristic photoelectric work function* in degrees Kelvin. If the values of w_p' are plotted against the corresponding temperatures T, a curve is obtained which has a generally *negative* slope. The data are shown in the left-hand group of lines in Fig. 1.

Only a slight temperature dependence of the measured values of B was noted, so that the effect of temperature on the absorption probability factor may be neglected.

The state of activation of the surfaces are described by "f numbers," which were determined from the observed thermionic work functions at 1274°K and the data of Brattain and Becker.[12] If these work functions are plotted against the corresponding f numbers the familiar parabola-like curve is obtained as seen in Fig. 3 (broken line). On the other hand, if the photoelectric work functions for 300° and 670°K are plotted against the same f numbers, straight lines with negative slopes result. (Solid lines of Fig. 3.)

According to the simple theory,[1] it would be expected that the photoelectric and thermionic work functions at a given temperature, as determined in the above manner, would be identical. This would mean that the low temperature (photoelectric) and high temperature (thermionic) portions of the work function plots of Fig. 1 would join together into a smooth line. For the cleanest surfaces ($f=0.16$) this condition is approximately fulfilled, within experimental error. The discrepancy between the photoelectric and thermionic data becomes progressively worse as thorium is added to the surface. In fact, for thoriated surfaces the temperature coefficients of the photoelectric and thermionic work functions are of opposite sign. Some reasons for this discrepancy must be found.

In the first place it seems evident that the discrepancy cannot be attributed to experimental error. Errors as large as 10 percent in reading the photoelectric and thermionic emission currents would have a negligible effect on the work function determinations; and the precision of current and light intensity measurements was considerably better than this for the most part. It is impossible to attribute any appreciable portion of the discrepancy to errors in the temperature scale. On the other hand, if one assumes the true emitting area of the filament to be greater than the apparent area by a factor of 1.3 (which appears to be a reasonable estimate[19–21]), the discrepancy between photoelectric and thermionic measurements become worse.

Another possible source of error is that due to the accumulation of impurities on the surface during the course of a day's run. Readings of the thermionic emission for a given activation were repeated, however, on the following days, and in every case the emission for a given temperature remained practically unchanged. The vacuum conditions were good enough, and the filament had been well aged and outgassed so that this result was not unexpected. Values of the photoelectric work functions, on the other hand, varied somewhat from one day to the next. This variation appears to be outside the total experimental error as seen in Fig. 1, but is still of the order of only one percent.

On the basis of the above observations, there is some evidence that a rearrangement of patches or a redistribution of thorium adatoms occurs with temperature and time. The differences between thermionic and photoelectric work functions, however, are not accounted for properly.

Since experimental errors are insufficient to explain the difference, the simple theory used for the reduction of the data must be examined. One could, of course, bring the data into agreement by inserting into Eq. (4) a suitably chosen value for the surface transmission coefficient. For example, the data for $f=0.68$ would reduce to a single smooth line of negative slope by assuming a *transmission* coefficient of approximately 5.0×10^{-3}. In view of other evidence relating to the values of electron reflection coefficients at metal surfaces this value appears unreasonably small. It appears necessary, therefore, to seek elsewhere to account for the major portion of the discrepancy.

Both the thermionic and photoelectric equations are deduced for clean, uniform surfaces. If however, W_a and W_i vary from point to point on the surface the equations will not be applicable to the emission from the whole surface. Work

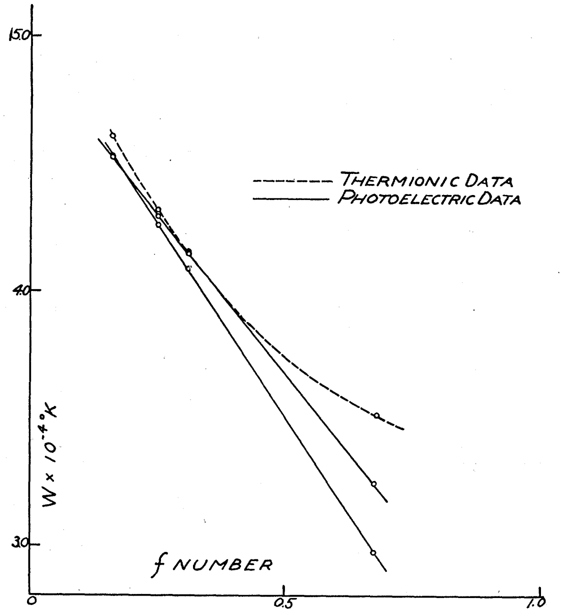

FIG. 3. Work function *versus* f numbers. The thermionic curve is plotted for a temperature of 1270°K; the upper photoelectric curve for 300°K; and the lower one for 670°K.

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[19] Tonks, Phys. Rev. **38**, 1030 (1931).

[20] Langmuir, J. Am. Chem. Soc. **54**, 2798 (1932).

[21] de Boer, *Electron Emission and Absorption Phenomena* (Cambridge, 1936), p. 72.

functions determined by means of these equations, therefore, will be average values for the whole surface and may be called "characteristic work functions." However, the thermionic and photoelectric emission equations are different in form, so that there is no reason to expect these average or characteristic work functions to be the same for the two processes or to show the same temperature dependence.

THEORY

In both the thermionic and photoelectric theoretical equations the work function w in degrees Kelvin is equal to $(W_a-W_i)/k$; in which W_a is the height of the surface barrier in energy units, W_i is an integration constant, and k is Boltzmann's constant. To a high degree of approximation W_i is given by the relation

$$W_i=(h^2/2m)\{3nf/4\pi G\}^{\frac{2}{3}},$$

where n is the number of atoms per cubic centimeter; f is the number of free electrons per atom, which is usually assumed to be equal to the number of valence electrons; and G is the statistical weight, which is equal to 2 for electrons. Since W_i depends upon n, which in turn may change with temperature, it follows that W_i is a function of temperature.

On the other hand, W_a should decrease in value as the distance between surface atoms is increased; hence, due to thermal expansion, the work function should decrease with rising temperature. Detailed calculations have been made by Bridgman,[22] Herzfeld,[23] and Wigner.[24] Experimental results have not been sufficiently precise, however, to indicate the correctness of these theories.

In any case, the above theories are developed for uniform surfaces. Composite surfaces, on the other hand, give rise to more complex phenomena. To explain the anomolous Schottky effect, for instance, Langmuir suggested that adatoms were grouped in patches which have a profound influence upon the thermionic emission at low accelerating fields.[25] This suggestion was developed by Linford[26] and Becker and Rojansky;[27] and later it was modified by Becker[28] and by Nottingham.[4] In the following discussion in which a phenomenological theory is described, patches are assumed to exist; but their exact nature is not investigated.

For any electron emission whatever, the current density is given by the relation

$$i=(1/A)\int_s i_s ds, \tag{5}$$

in which ds is an element of the total emitting area A and i_s is the current density of that element. The assumption will now be made that the element ds is clean and pure, so that the Richardson-Dushman or the Fowler equation may be applied to it, depending upon whether the emission is thermal or photoelectric. The further assumption is made that the field is such that all the electrons are collected by the anode.

For the thermionic case i_s is given by the relation

$$i_s=UT^2e^{-w_s/T}, \tag{6}$$

in which U is the universal constant (1), and w_s is the surface work function, which is assumed to vary from point to point, i.e.,

$$w_s=T\left\{a+b\cos\frac{\pi x}{t}\cos\frac{\pi y}{r}\right\}. \tag{7}$$

Here a and b are functions of temperature and applied field, and t and r are the lengths of the sides of a single rectangular patch. All values of w_s are found over the area $\frac{1}{2}tr$, so that upon insertion of the above relations in Eq. (5) the integration may be extended from $x=y=0$ to $x=t/2$ and $y=r$. That is

$$i=\frac{2}{tr}UT^2e^{-a}\int_0^{t/2}\int_0^r \exp\left[-b\cos\frac{\pi x}{t}\cos\frac{\pi y}{r}\right]dx\,dy, \tag{8}$$

in which A has been replaced by $\frac{1}{2}tr$.

The exponential under the integral sign now is expanded in a Taylor's series and integrated term by term. There results

$$i=UT^2e^{-a}S(b), \tag{9}$$

in which $$S(b)=1+\sum_{n=1}^{\infty}\frac{(2n)!}{2^{4n}(n!)^4}b^{2n}. \tag{10}$$

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[22] Bridgman, Phys. Rev. **31**, 90, 862 (1925).

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

[24] Wigner, Phys. Rev. **49**, 696 (1936).

[25] Langmuir, Gen. Elec. Rev. **23**, 503, 589 (1920).

[26] Linford, Phys. Rev. **37**, 1018 (1931) and reference 7.

[27] Becker and Rojansky, see footnote of reference 7, p. 50.

[28] Becker, Rev. Mod. Phys. **7**, 95 (1935).

This series is convergent for all finite values of b. Values of $S(b)$ and $\log S(b)$ are given in Table I.[29]

The observed total emission i may be assumed to obey an equation similar to (6). That is

$$i = UT^2 e^{-w/T}. \tag{11}$$

in which w has already been called the characteristic thermionic work function of the surface. Substitute this value of i in Eq. (9) and take logarithms. Then

$$w = aT - 2.303T \log S(b). \tag{12}$$

From Eq. (7) it is evident that

$$a = (w_{\max} + w_{\min})/2T \tag{13}$$

and

$$b = (w_{\max} - w_{\min})/2T. \tag{13'}$$

In this manner the measured work function has been related to the temperature and the maximum and minimum values of w. Already one important conclusion may be drawn; namely the characteristic thermionic work function is independent of the size of the patches. By means of a different method of analysis Becker came to the same conclusion.[28]

If now the derivative of w with respect to temperature is taken, there results

$$\frac{dw}{dT} = \frac{1}{2}\left\{1 - \frac{b}{2}\frac{R(b)}{S(b)}\right\}\frac{dw_{\max}}{dT} + \frac{1}{2}\left\{1 + \frac{b}{2}\frac{R(b)}{S(b)}\right\}\frac{dw_{\min}}{dT} - 2.303 \log S(b) + \frac{b^2}{2}\frac{R(b)}{S(b)}, \tag{14}$$

TABLE I. *Values of functions $S(b)$ and $R(b)$.*

b	$S(b)$	LOG $S(b)$	$R(b)$
0	1.000	0	0.5000
1	1.131	0.0535	0.5485
2	1.603	0.2049	0.7155
4	5.197	0.7157	1.813
6	23.57	1.3724	6.250
8	127.7	2.1064	1.4405
10	742	2.8704	132.5
12	4521	3.6552	
15	7.188×10^4	4.8566	8914
20	7.928×10^6	6.8992	

in which

$$R(b) = \frac{2}{b}\frac{dS(b)}{db} = \frac{1}{2}\left\{1 + \sum_{n=1}^{\infty}\frac{(2n)!(2n+1)}{2^{4n}(n!)^4(n+1)^2}b^{2n}\right\}. \tag{15}$$

Values of $R(b)$ are given in Table I.

A similar operation is now carried out for the photoelectric aspect of the problem. In this case

$$i_s = \beta_s U T^2 \varphi(x_s), \tag{16}$$

in which β_s is the absorption probability and

$$\varphi(x_s) = \frac{x_s^2}{2} + \frac{\pi^2}{6} + \sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}e^{-nx_s} \tag{17}$$

for $x_s \geqslant 0$; and

$$\varphi(x_s) = -\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}e^{nx_s} \tag{17'}$$

for $x_s \leqslant 0$ where

$$x_s = h\nu/kT - w_s/T.$$

If now β_s is assumed to be independent of the surface condition, frequency, and temperature in the neighborhood of the threshold;

$$\varphi(x) = \frac{1}{A}\int_s \varphi(x_s)\cdot ds. \tag{18}$$

In Fig. 4 is plotted the diagram of a single patch over which the work function is given by Eq. (7). Maximum values of w occur at $x=0$, $y=0$ and $x=t$, $y=r$. Minimum values occur at $x=0$, $y=r$ and $x=t$, $y=0$. Contours of equal values of w are shown in Fig. 4 at M, N, etc. Evidently the pair of bisecting lines AB and CD are loci of points at which

$$w = (w_{\max} + w_{\min})/2 = aT.$$

It is clear that if $h\nu/k > w_{\max}$ then Eq. (17) must be used; and if $h\nu/k < w_{\min}$ Eq. (17′) must be used. On the other hand, if $w_{\min} < h\nu/k < w_{\max}$, then Eq. (17) is used for that portion of the patch for which $x_s > 0$ and (17′) for that portion for which $x_s < 0$. Since the general solution of the problem is rather difficult and involves an extra parameter, only three special cases will be discussed.

(1) For $h\nu/k = w_{\max} = T(a+b)$,

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[29] Values of $S(b)$ were calculated from the series:

$$S(b) = 1 + 0.125b^2 + 5.859\times10^{-3}b^4 + 1.356\times10^{-4}b^6 + 1.854\times10^{-6}b^8 + 1.669\times10^{-8}b^{10} + 1.062\times10^{-4}b^{12} + 5.033\times10^{-13}b^{14} + 1.843\times10^{-15}b^{16} + 5.373\times10^{-18}b^{18} + 1.276\times10^{-20}b^{20} + 2.517\times10^{-23}b^{22} + 4.187\times10^{-26}b^{24} + 5.956\times10^{-29}b^{26} + 7.325\times10^{-32}b^{28} + 7.868\times10^{-35}b^{30} + 7.428\times10^{-38}b^{32} + 6.240\times10^{-41}b^{34} + 4.674\times10^{-44}b^{36} + 3.159\times10^{-47}b^{38} + 1.925\times10^{-50}b^{40}.$$

Coefficients of the terms in which $n > 15$ were calculated by means of the relation: $2.303 \log C_n = 2n(0.3068 - 2.303 \log n) - 3.4539 \log n - 2.4103 - 7/24n$. The series $R(b)$ is related to $S(b)$ by Eq. (15).

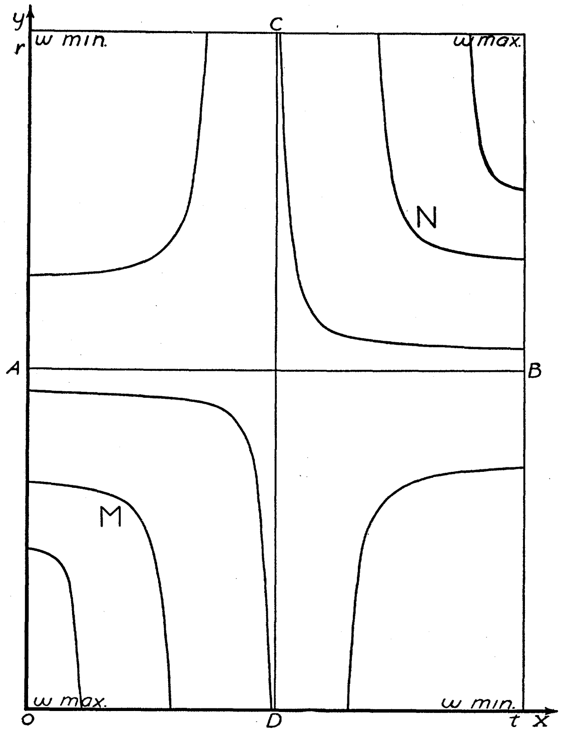

FIG. 4. Diagram of a single patch over which all values of the work functions from w_{min} to w_{max} exist. Curves such as MN represent loci of points on the surface where a given work function is found.

$$\varphi(x)=\frac{2}{tr}\int_0^{t/2}\int_0^{r}\left\{\frac{b^2}{2}\left(1-2\cos\frac{\pi x}{t}\cos\frac{\pi y}{r}+\cos^2\frac{\pi x}{t}\cos^2\frac{\pi y}{r}\right)+\frac{\pi^2}{6}+\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}e^{-nb}\cdot\exp\left[nb\cos\frac{\pi x}{t}\cos\frac{\pi y}{r}\right]\right\}dxdy$$

$$=\frac{5b^2}{8}+\frac{\pi^2}{6}+\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}e^{-nb}S(nb),\tag{19}$$

in which $S(nb)$ is the same series that occurred in the thermionic equations.

(2) For $h\nu/k=w_{\text{min}}=T(a-b)$

$$\varphi(x)=-\frac{2}{tr}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}e^{-nb}\int_0^{t/2}\int_0^{r}\cdot\exp\left[-nb\cos\frac{\pi x}{t}\cos\frac{\pi y}{r}\right]dxdy$$

$$=-\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}e^{-nb}S(nb).\tag{20}$$

(3) For $h\nu/k=(w_{\text{max}}+w_{\text{min}})/2=aT$

$$\varphi(x)=\frac{2}{tr}\int_0^{t/2}\int_{r/2}^{r}\left\{\frac{b^2}{2}\cos^2\frac{\pi x}{t}\cos^2\frac{\pi y}{r}+\frac{\pi^2}{6}+\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left[nb\cos\frac{\pi x}{t}\cos\frac{\pi y}{r}\right]\right\}dxdy$$

$$-\frac{2}{tr}\int_0^{t/2}\int_0^{r/2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\cdot\exp\left[-nb\cos\frac{\pi x}{t}\cos\frac{\pi y}{r}\right]dxdy$$

$$=\frac{b^2}{16}+\frac{\pi^2}{12}.\tag{21}$$

Since (21) is always positive it is apparent that $h\nu/k=(w_{\text{max}}+w_{\text{min}})/2$ must always be above the threshold for composite surfaces. Usually this value of the frequency lies near the threshold; so that for a given b it is possible to solve for x and thereby obtain a value of w from

$$w=T(a-x),\tag{22}$$

where w has already been termed the characteristic photoelectric work function.

Equations (12) and (22) can be identical for a given temperature only if

$$x=2.303\log S(b)\tag{23}$$

for which Eq. (21) is satisfied. This condition obtains for $b=0$. Thus *the thermionic and photoelectric work functions are equal only in the case of a uniform surface or for a composite surface at extremely high temperatures.*

By differentiating Eq. (22) with respect to temperature there results

$$\frac{dw}{dT}=\frac{1}{2}\left(1-\frac{b}{8}\frac{dx}{d\varphi}\right)\frac{dw_{\text{max}}}{dT}+\frac{1}{2}\left(1+\frac{b}{8}\frac{dx}{d\varphi}\right)\frac{dw_{\text{min}}}{dT}-x+\frac{b^2}{8}\frac{dx}{d\varphi},\tag{24}$$

in which

$$d\varphi/dx=2.303\log(1+e^x),\tag{25}$$

where x is related to b by Eq. (21). Eqs. (14) and (24) are identical for a given temperature when the coefficients of dw_{max}/dT and dw_{min}/dT are the same in the two equations. Only $b=0$ will satisfy these conditions. Thus *the temperature coefficients of the thermionic and photoelectric work functions are identical only for uniform surfaces or for composite surfaces at extremely high temperatures.*

From these results it follows that the thermionic and photoelectric work function versus temperature curve for composite surfaces must differ from one another at low temperatures and approach each other asymptotically at high temperatures.

Without a knowledge of either $w_{\max}$ or $w_{\min}$ it is difficult to carry out any calculations of a quantitative nature. Becker states that $2\mu=0.88$ electron volts for $f=0.33$ and $T=1270°\mathrm{K}$; that is, $w_{\max}-w_{\min}=10{,}270°\mathrm{K}$ and, therefore $b=4.045$. If it is assumed that $dw_{\max}/dT$ and $dw_{\min}/dT$ are constants and an attempt is made to evaluate them by trial and error in terms of the above reported data for $f=0.31$, no values will satisfy the theoretical equations. This result indicates that $dw_{\max}/dT$ and $dw_{\min}/dT$ may be functions of temperature.

CONCLUSION

The above analysis has been given in some detail since it leads to the important conclusion that for nonuniform surfaces in general simultaneous measurements of the photoelectric and thermionic work functions will not be expected to yield values which are equal or which show the same temperature coefficient. The experimental measurements reported herein constitute an excellent example. A similar argument could be extended to contact potential measurements since these involve a still different type of averaging over the surface. We thus find that values of α deduced from thermionic measurements and Eq. (4) cannot be checked by other measurements except for surfaces over which the work function is uniform. Reimann[4a] has recently found this expected lack of agreement between values of α deduced from Eq. (4) and from contact potential measurements, but he attributes the difference to a reflection coefficient. Our analysis would indicate that this is not justified.

Furthermore, as is seen from Eq. (14), thermionic measurements will yield an apparent temperature coefficient of w even for patched surfaces for which the work function at each and every point is actually independent of temperature. This is because the relative contribution of individual areas to the total emission will change with temperature. Consideration of the numerical values in Table I shows that in this case α will be positive and hence $A<U$, as is nearly always observed.

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