

ON ELECTRICAL FIELDS NEAR METALLIC SURFACES

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ABSTRACT

When an electron escapes from a metallic surface it passes through fields which tend to pull it back. Properly directed applied fields partially neutralize the surface fields and hence reduce the work the electron has to do against these fields. That is why i , the thermionic current, increases steadily with F_a , the applied field. Quantitatively $d(\log_{10} i)/dF_a = (11600/2.3 T) \times s$, where T is the temperature of the surface and s is the distance from the surface at which the surface field F_s is equal to F_a . Hence the slope of an experimental $\log i$ vs F_a curve at any F_a yields the value of s corresponding to F_a . For clean or atomically homogeneous surfaces experiment shows that the only force opposing the escaping electron is due to its image field; for composite surfaces other fields, which are ascribed to the adsorbed ions, are superposed on the image field. For 70 percent thoriated tungsten this "adsorption field" is very large close to the surface and in a direction to help electrons escape; it decreases rapidly in strength as s increases until it is zero at about 15 atom diameters; here it reverses its direction and then increases in strength till it attains a maximum value of 8000 volts/cm at 75 atom diameters; beyond this distance it decreases steadily. The intense field close to the surface accounts for the decreased *work function* while the reverse field farther out accounts for the poor saturation at ordinary applied potentials.

The photo-electric long wave-length limit should be shifted toward the red by applied fields. This shift should be particularly noticeable for composite surfaces.

IT IS a matter of common observation that the thermionic current flowing from a heated filament to a nearby anode is never entirely independent of the anode potential. No matter how great a potential difference is applied between filament and anode, a further increase in this potential difference is invariably accompanied by an increase in current. This failure of the thermionic current to saturate with anode potential or this lack of saturation is not very pronounced for homogeneous surfaces such as, for example, clean tungsten. If, however, this surface is partially covered with adsorbed electropositive atoms such as thorium or caesium, the thermionic current from the resulting composite surface saturates very poorly with anode potential. When the tungsten surface is completely covered with a layer of the adsorbed atoms, the lack of saturation is no longer very marked. This effect is illustrated quantitatively in Fig. 1 which shows how the emission current varies with the plate potential for three surfaces. The currents have been multiplied by proper constants such that all three curves pass through the same point for a plate potential of 100 volts. The dashed curve represents the current vs. voltage or i vs. V relation for a clean tungsten filament. The curve marked $\theta = 17$ is an experimentally observed i vs. V curve for a tungsten filament whose surface is partially covered with oxygen and with caesium. θ is the percentage of the surface covered with caesium. The third curve marked $\theta = 120$ is an experimental curve for the same oxidized

tungsten filament when the surface is covered with enough caesium to form 1.2 atomic layers. Note that for a clean tungsten filament the current saturates quite well; when the surface is partially covered with caesium the saturation is very poor indeed; but when the surface is somewhat more than completely covered with caesium the saturation is quite good again. This phenomenon cannot be ascribed to the ionization of gas that may exist between the cathode and anode. Neither can the shape of the $\theta = 17$ curve be explained by the hypothesis that the current is limited by space charge for the largest current is less than 25 microamperes and the structure of the tube is such that a fraction of a volt applied to the plate should produce saturation. The $\theta = 17$ curve illustrates a very striking case of poor saturation. Numerous intermediate stages have been observed in this laboratory in tubes of various shapes and character of filament. *There can be no doubt that this marked failure to saturate is associated with adsorbed electropositive atoms which partially cover electronegative metal surfaces.*

What is the cause of this lack of saturation for composite surfaces? Obviously the applied potential must help electrons escape which otherwise would fail to free themselves from the influence of the surface. It could do this if, in their escape, the electrons had to pass through electrical fields which tended to pull the electron back into the surface. An analysis which follows shows in detail that such a hypothesis does satisfactorily account for the lack of saturation. More than this, it shows just *how to determine the strength of these fields at various distances from the surface.* Before giving this analysis it is desirable to discuss the only published quantitative theory bearing on the lack of saturation and to show that it is inadequate to account for the lack of saturation for composite surfaces.

SCHOTTKY'S THEORY

In 1914 Schottky¹ proposed the hypothesis that when an electron escapes from a metallic surface it induces thereon a charge equal in magnitude but opposite in sign to its own charge, and that the force between these charges prevents the free escape of the electron. This force is given by the well-known image equation $F_e = e^2/4s^2$ where F is the induced field acting on the electron and s is the distance from the surface to the electron. The thermionic "work function" is interpreted quite simply as the work done against this image force in transferring an electron from the surface to an infinite distance from it. When $s=0$, $F = \infty$ and the integral of Fds is also infinite. To avoid this difficulty, Schottky postulated that the force is constant and equal to $e^2/4s_c^2$ from $s=0$ to $s=s_c$, a distance characteristic of the metal, but that beyond s_c the force is given by the image equation. It follows from this that half the work function is used in getting to s_c and the other half in going beyond s_c .² The values of s_c corresponding to ordinary work functions of 2 to 8 volts are 4 to 1×10^{-8} cm respectively, that is, s_c is of the order of atomic dimensions.

¹ W. Schottky, Phys. Zeits. 15, 872 (1914).

On the basis of his hypothesis Schottky showed that if a potential gradient is applied at the surface of a filament, an electron need not have as much energy as before in order to escape from the filament, and that consequently the emission current should increase with the applied potential. The relation to be expected between current and potential gradient is given quantitatively by his equation:

$$\log_{10} i = \log_{10} i_0 + 4.39(cV)^{1/2}/2.3T \quad (1)$$

in which i is the thermionic current in amperes/cm² for the variable plate potential V in volts; $i_0 = i$ when $V = 0$; T , the absolute temperature of the filament; and c the constant, determined by geometry, by which V is multiplied to give the potential gradient at the surface of the filament.

Schottky also showed experimentally that $\log i$ for clean tungsten at 1300°K increased linearly with $(cV)^{1/2}$ for values of cV from 10,000 to 50,000 volts/cm and that the rate of increase was within 20 percent of the rate given by Eq. (1). The 20 percent discrepancy could plausibly be accounted for by imperfections in his tube. Since then, no one seems to have made a thorough and careful test of Eq. (1) but many observers must have verified its approximate truth. If it is indeed true, it furnishes strong evidence that

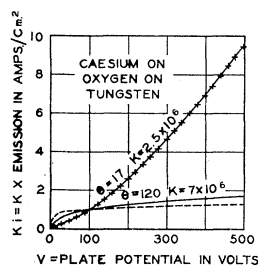


Fig. 1

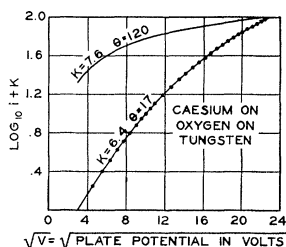


Fig. 2

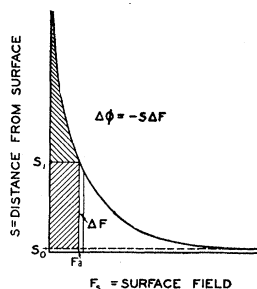


Fig. 3

Fig. 1. The dashed curve is for clean tungsten. The other two are for caesium on oxygen on tungsten. θ gives the percentage of the surface covered with caesium.

Fig. 2. This shows that the current from composited surfaces does not follow Schottky's equation.

Fig. 3. This is a sketch to illustrate the decrease in the work function ϕ produced by a change in the applied field F_a , when a surface field F_s tends to pull the electron back into the surface.

beyond some small distance from the surface the forces on the electron are image forces and no others. This satisfactorily explains the lack of saturation in clean surfaces.

Since the current voltage curves for composite surfaces differ markedly from those for clean surfaces as is illustrated in Fig. 1, it is impossible that Schottky's law given by Eq. (1), can apply in such cases. Numerous tests

² This looks like an arbitrary assumption, and actually is unnecessary. We shall show later that it is possible to arrive at Schottky's conclusions by merely assuming that the image law holds for distances beyond about 40 atom diameters. It is unnecessary to make any assumption about the law of force at closer distances.

have shown that $\log i$ for such filaments does not vary linearly with $V^{1/2}$ if a sufficiently large range of voltages is investigated. Even when the relation is approximately linear over a small range the slope of the curve differs markedly from that for clean surfaces. Furthermore the ranges of linearity and the slopes change when the amount of surface impurities changes. As an illustration, Fig. 2 shows a plot of $\log i$ vs. $V^{1/2}$ for the data shown in Fig. 1. Note that the curve for $\theta=17$ is nowhere linear over an appreciable range while that for $\theta=120$ is quite linear at the higher voltages. Even here the slope is about twice as great as we estimate it should be for the same filament with a clean tungsten surface. For the $\theta=17$ curve the mean slope is about ten times what Schottky's equation requires. It is clear, then, that Schottky's theory does not account for the observed saturation curves for composite surfaces.

A METHOD OF MEASURING SURFACE FIELDS

To seek the cause of the very poor saturation curves for composite surfaces we can proceed as follows: The emission from a filament obeys Richardson's equation of the type

$$\log_{10} i = \log_{10} A + n \log_{10} T - \phi e / 2.3kT \quad (2)$$

where i is the observed current; A is a constant that appears in the thermodynamic argument which leads to Richardson's equation (its value involves numerical constants as well as the well-known constants of nature k , m , e , and h); n is a number which in specific forms of this equation has the value 0 , $\frac{1}{2}$, or 2 ; T is the absolute temperature of the filament; ϕ , the work function; e , charge on electron; k , Boltzmann's constant.

Since the current varies with F_a , the applied field near the surface of the filament, we can differentiate (2). Assuming that A does not vary with F we obtain:

$$\frac{d(\log_{10} i)}{dF_a} = \frac{-e}{2.3kT} \frac{d\phi}{dF_a} \quad (3)$$

This means that the slope of the experimental $\log i$ vs F_a curve gives us $d\phi/dF$, the rate at which the work function is being reduced at that field strength. But $d\phi/dF$ is simply related to the s vs F_s curve, where F_s is the surface field which pulls the electron toward the surface when the electron is at a distance s from the surface.

Fig. 3 is a sketch of a general form of such a curve. The surface is defined as the loci of the outermost positive nuclei. The distance s_0 is the greatest distance the electrons can get from this surface and still remain in their orbits. The area to the left of this curve from $s = \infty$ to $s = s_0$ represents that part of ϕ which is due to the surface fields. If we now apply a field F_a there will exist a distance s_1 at which F_a counterbalances F_s and the net field is zero. Beyond s_1 the net field pulls the electron out while inside s_1 the net field pulls it in. Any electron which now reaches s_1 will permanently escape. The work function is reduced for two reasons: (1) while the electron

is going from s_0 to s_1 the applied field is helping it out—this is represented by the shaded area between s_0 and s_1 ; (2) the electron need not have sufficient energy to overcome the forces represented by the shaded area beyond s_1 . In general if the field is increased from any value F_a to $F_a + \Delta F$, the work function is decreased by an amount corresponding to the area $s\Delta F$; or $\Delta\phi = -s\Delta F$; or

$$\Delta\phi/\Delta F = -s \text{ and in the limit } d\phi/dF = -s \quad (4)$$

Substituting this in (3):

$$d(\log_{10} i)/dF = es/2.3kT = 11600s/2.3T \quad (5)$$

Hence *the slope of the log i vs F_a curve at any F_a tells us the distance s from the surface at which the applied field equals the surface field, F_s* . Thus we can readily determine the fields that exist near the surfaces of metals for all regions for which we can neutralize these fields by applied fields.

CRITICAL DISCUSSION

It should be pointed out that the shape of the saturation curves is determined by the value of F beyond s_1 and not at all by its value inside of s_1 . Consequently it was unnecessary for Schottky to particularize his theory by assuming that half the work function was used up against image fields and the other half against a constant field very close to the surface. The final deduction is the same no matter what kind of field exists very close to the surface.

In deriving equation (4) it was tacitly assumed that the applied field was uniform from s_0 to s_1 . For a smooth surface this would quite likely be true for all values of s that are of appreciable importance. Since filaments are not smooth this assumption might cause serious difficulties. If we could compute the field distribution due to an applied potential, near a rough spot we could still apply the present method. The element of area in Fig. 3 would no longer have vertical sides nor constant width but its area could still be computed. This would modify equations (4) and (5). However, for applied fields less than about 100,000 volts/cm and for ordinary non-uniformities this modification is likely to be negligible. A field of 100,000 volts/cm will neutralize an image field at $s_1 = (300 \times 4.8 \times 10^{-10} / 4 \times 10^5)^{1/2}$ or 60×10^{-8} cm. For these conditions, the image field, the applied field and the element of area in Fig. 3 will have about the same value they would have if the roughness were removed. Furthermore Schottky actually found that experiment gave agreement with the image law even for fields of 500,000 volts/cm. Hence ordinary rough spots on the surface do not introduce appreciable errors for ordinary potentials.

Another tacit assumption is that s_0 , the largest distance an electron orbit extends from the surface, does not change with the applied field. This too is quite likely for fields less than 10^5 volts/cm, since the fields existing near the electron orbits must be of the order of 10^5 volts/cm. The orbits should therefore be inappreciably influenced by these applied fields. For larger

fields we must expect s_0 to be increased and hence ϕ decreased by the applied field. This is probably the cause of the cold discharge due to intense fields.

By experimentally obtaining $\log i$ vs F_a curves at various temperatures it is possible to determine s vs F_s curves at these temperatures and consequently determine whether the area underneath them or the corresponding part of the work function is independent of temperature. If F_s is due solely to the image forces, there should be but one s vs F_s curve for all temperatures and the slope of the $\log i$ vs $V^{1/2}$ curves multiplied by T should give a constant. Dushman³ has shown this to be an experimental fact for clean tungsten.

APPLICATION OF METHOD: AN ILLUSTRATION

The authors are applying the method to determine a series of s vs F_s curves for thoriated tungsten from a series of experimentally determined $\log i$ vs V curves for various values of θ and for various values of T at each θ . From the s vs F_s curves we hope to determine: (1) how much they deviate from the image equation; (2) how this deviation varies with θ ; (3) whether the surface fields at a given θ are altered by a change in temperature, that is, whether for thin films $d\phi/dT=0$ as it seems to be for clean surfaces. The

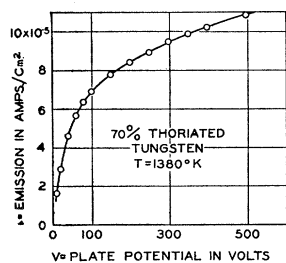


Fig. 4

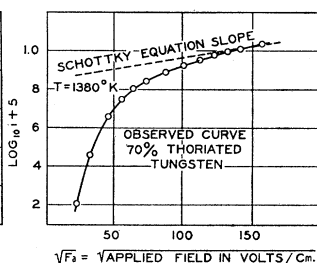


Fig. 5

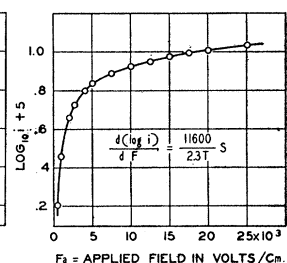


Fig. 6

Fig. 4. This shows that the current from a 70% thoriated tungsten filament saturates poorly.

Fig. 5. This shows that the current does not follow Schottky's equation at low and moderate applied fields.

Fig. 6. The slope of this curve at any value of F_a gives s , the distance from the surface at which the surface field F_s is equal to that particular value of F_a .

s vs F_s curves may also yield quantitative information about: (1) the electrical doublets resulting from the adsorbed thorium; (2) how many of the adsorbed thorium atoms have given up their valence electrons to the surface to become surface ions; (3) whether the number of surface ions at a given θ varies with the temperature as is required by Boltzmann's principle if a surface ionization potential exists. It should also be profitable to study other electropositive materials than thorium, as well as electronegative materials like oxygen, by the same methods and with the same viewpoints.

For all this work the s vs F_s curves are essential. In order to give a concrete illustration of what such a curve is like and the data on which it is

³ S. Dushman et al. Phys. Rev. 25, 346 (1925).

based we are including Figs. 4, 5, 6, and 7. Fig. 4 shows an experimental i vs V curve for a 70 percent thoriated tungsten filament 0.0086 cm (3 mils) in diameter stretched along the axis of three nickel cylinders 1.47 cm in diameter. Note the poor saturation. Fig. 5 shows that the observed points do not fall on a straight line on a $\log i$ vs $F^{1/2}$ plot and that the slope is considerably greater than that given by Schottky's equation. Note, however, that at the higher potentials the observed curve is more nearly straight and its slope is only slightly greater than Schottky's theory requires. Fig. 6 shows the same data in a $\log i$ vs F_a plot. F_a in volts/cm near the surface of the

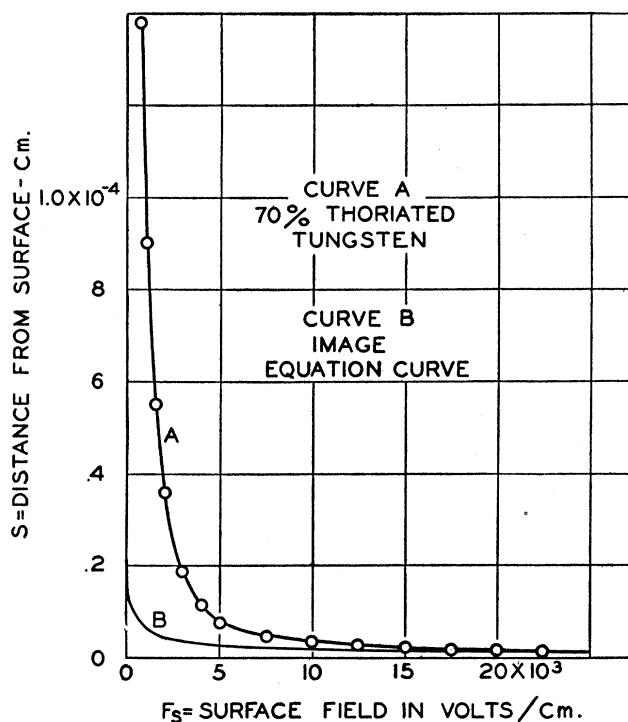


Fig. 7. This shows that the fields near a composite surface differ greatly from those near a homogeneous surface for which they vary according to the image equation. At any s the difference between F_s for curves A and B gives the field due to the adsorbed thorium.

filament is 50 times the plate potential in volts. The slope of this curve at any F_a gives s , the distance from the surface at which the surface field, F_s , equals the applied field, F_a . Finally Fig. 7 shows the s vs F_s curve for 70 percent thoriated tungsten together with the image equation curve, $F = e/4s^2$.

This is the most important figure in this group and hence it warrants some discussion. In a certain sense curve B does not represent a true surface field, since the field does not exist unless the electron under consideration is at a distance s from the surface. Nevertheless the force on the electron

can be spoken of as due to its induced field and it is in this sense that we use the term. Most likely when the electron escapes from the thoriated surface it does work against its image field. Hence at any s it is only the difference between F_s for curve A and curve B which represents the true field which is caused by the presence of the adsorbed thorium. It is very striking that this adsorption surface field has appreciable values at such large distances from the surface. Thus at a distance of 1×10^{-4} cm or 2500 thorium atom diameters away from the surface the field due to the thorium is still 1000 volts/cm; at 1×10^{-5} cm or 250 diameters it is approximately 4000 volts/cm; at 3×10^{-6} cm or 75 diameters it is approximately 8000 volts/cm. Then for still closer distances the field decreases until at something like 6×10^{-7} cm or 15 diameters the field is zero. At all these distances the direction of the field is such as to tend to pull the electron back into the surface. For still closer distances Fig. 7 suggests that the field must rapidly become very large but in a direction to help the electron escape. The net effect of the fields due to the thorium must be to help the electrons escape since the work function of thoriated tungsten is less than that of clean tungsten. Hence curve A must go below B for small values of s . This can be tested by using higher applied potentials or filaments of a smaller diameter. In some preliminary tubes we have actually observed cases in which the A curve crossed the B curve at the higher potential gradients. Since $d(\log i)/dF$ is proportional to s , this means that at high enough potentials, thoriated tungsten saturates as well as or better than clean tungsten. To sum up the picture to which we are led: *the adsorbed thorium or other electropositive material produces fields which close to the surface are very large and in such a direction to help electrons escape; at larger distances the fields are in the opposite direction and may be of appreciable magnitude as far out as 2500 thorium atom diameters.* The huge fields close to the surface are responsible for the decreased work function while the reverse fields farther out are the cause of the marked lack of saturation at ordinary applied potentials.

The fields due to the thorium which are in a direction to hinder the escape of the electrons are astoundingly large at fairly large distances from the surface. They are much larger than one would expect if the thorium ions are rigidly fixed on the surface. It may be that in order to account for these fields, one must assume that an ion is ejected to various distances from the surface by thermal impacts and is pulled back by surface forces. The average distance of all the ions at any one instant may be several times the ion radius and hence the fields produced by these ions may be appreciable at considerable distances from the surface. In the case of caesium on tungsten, some caesium ions are pushed to such large distances from the surface that they are no longer pulled back but permanently escape. Another way to account for these fields is to assume that a composite surface carries a net positive charge. It should also be pointed out that for composite surfaces the A in Richardson's equation may not mean quite the same thing as it does for homogeneous surfaces. Hence it may be that A for composite

surfaces may vary when the applied field is varied which is contrary to the assumption that was made in deriving Eq. (3) above. Whatever the explanation for the fields in question may be, we feel that a fuller discussion had better be left until the present method has been applied to a series of values of θ and T for thorium on tungsten. For the present we wish merely to point out that the surface fields obtained by this method are of such striking magnitude that they require an explanation and that quite likely when we have found this explanation we shall know more about the mechanism of emission from composite surfaces.

In the meanwhile it may not be amiss to point out how the views presented here will modify the conclusions reached in a recent paper on "Electron Emission from Thoriated Tungsten" by Dushman and Ewald⁴. In this paper they computed the current that should be emitted at zero applied potential by assuming that Schottky's equation held for all thoriations and for all applied potentials. As a justification they state "More recent work by Mr. N. B. Reynolds in this laboratory (General Electric Company) has shown that Eq. (4) (which is the same as Eq. (1) above) is also applicable to thoriated tungsten filaments for field strengths which are many times greater than those worked with in the present investigation." Fig. 5 of the present article shows that the emission does approximately follow Schottky's equation at high field-strengths but that it deviates more and more at medium and low field-strengths. It looks as if the field-strength would be about one-tenth that obtained by extrapolating the Schottky line for high field-strengths. Furthermore, the difference between the extrapolated and true currents at zero field-strength will vary with θ and probably also with the temperature. To determine the emission characteristics for zero field-strength it will be necessary to empirically extrapolate the observed values of the current at various low field strengths for each θ and at each temperature and use these in the customary manner; or else to determine A and ϕ_0 for each of a series of low field-strengths and extrapolate the A and ϕ_0 values to zero field-strength. When this is done it may very well be that the A for completely activated thoriated tungsten ($\theta=0$) will be found to have the same value as for clean tungsten i.e., 60.2 amps/cm² deg¹.

We should like to point out also that the photo-electric current should be affected by the surface fields in a somewhat similar manner to the thermionic current. It is easy to see that the photo-electric current too should saturate poorly for partially covered surfaces, and that the long wave-length limit should shift toward the red when the applied field is increased from a small value to a larger value. This shift should be more pronounced for partially covered surfaces than for clean or completely covered surfaces. It seems probable that the details of the surface fields can more simply be ascertained from photo-electric than from thermionic effects. An excellent beginning of an experimental study of the photo-electric effects from composite sur-

⁴ Dushman and Ewald, Phys. Rev. 29, 857 (June 1927).

faces has been made in this laboratory by Dr. H. E. Ives and his collaborators.⁵

In conclusion we gratefully acknowledge the criticisms of Dr. W. Wilson and especially Dr. C. J. Davisson which have added to whatever merits this article may have.

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⁵ See particularly "Photoelectric Properties of Thin Films of Alkali Metals" by H. E. Ives, *Astrophysical Journal* **60**, 209-231 (1924).