SCHOTTKY EFFECT AND CONTACT POTENTIAL MEASUREMENTS ON THORIATED TUNGSTEN FILAMENTS

By Neil B. Reynolds
Palmer Physical Laboratory, Princeton University

(Received December 7, 1929)

Abstract

The Schottky effect for thoriated tungsten filaments is investigated and Schottky's relation that $\log i \propto (V)^{1/2}$ is verified at high fields, but fails at gradients below 10000 volts/cm, even for fully activated surfaces. This lack of saturation at low fields is accentuated by the effect of bombardment with high velocity positive ions, such bombardment apparently producing a surface roughening and consequently increased fields in local areas. Investigation with low accelerating and retarding voltages, while varying the temperature and state of activation of the filament, allows a comparison of the contact potential and the work function at the absolute zero of temperature (ϕ_0) for the thoriated surface. The two values (contact potential and ϕ_0) are found to vary with a one-to-one correspondence if ϕ, the work function at the temperature of measurement, be allowed a temperature coefficient. This coefficient is much larger than can be attributed to the specific heat of the electrons in the metal. The electrons with high velocities show a Maxwellian velocity distribution. Near the zero of potential there are certain anomalous effects and a "patch surface" is postulated which, in a qualitative manner, explains this behavior and the lack of current saturation with voltage gradients below a limiting value.

SCHOTTKY,[1] many years ago, derived an equation to explain the increase of saturation thermionic current with anode voltage. This relation has been verified by many investigators for pure metallic electron emitters, especially in the last few years. With one or two exceptions, the analogous effect with composite cathodes has been neglected, and the present paper deals with the current-voltage relations for thoriated tungsten filaments over a range of anode potentials from retarding potentials of 10 volts to accelerating potentials of 5000 volts, corresponding to potential gradients of nearly 500000 volts/cm.

A number of tubes were used in these experiments, varying slightly in detail but of the same general design. A 1.6 mil thoriated tungsten filament was stretched in the center of a cylindrical nickel or molybdenum anode. This was constructed in three pieces, on the guard ring principle. An alkaline earth metal was vaporized on the wall of the tube as a getter. The tube was given the best possible exhaust, baked, the metal parts degassed, and then sealed off from the pumping system. The tube was so designed that it could be completely immersed in liquid air.

The temperature of the filament was determined from the watts input according to the latest temperature scale of Jones.[2] Since all three parts of the

[1] W. Schottky, Phys. Zeits. **15**, 872 (1914); also Zeit. f. Physik **14**, 63 (1923).
[2] H. A. Jones, Phys. Rev. **28**, 202 (1926).

anode were maintained at the same potential but currents were measured only to the center cylinder, the effects of filament cooling at the leads and of field distortion at the edges were eliminated. Currents were measured by galvanometers and a Rawson multimeter, with a system of shunts giving a measuring range from 1 ampere to 5×10^{-11} amperes. Batteries, a 1500 volt dc generator and a 20000 volt full wave rectifier gave a complete range of anode potentials.

Langmuir and others[3] have described the methods of manipulation of thoriated tungsten cathodes. In these experiments the state of activation of the filament was controlled by allowing thorium to diffuse to the surface at lower temperatures, or by raising the temperature and removing it by evaporation. It is practically impossible to obtain a completely deactivated thoriated filament even by flashing at very high temperatures since diffusion occurs while the filament is cooling. In the present instance it was possible to obtain values of θ as low as 0.30 (θ = fraction of the surface covered).

Becker[4] has distinguished between the amount of barium present on a tungsten filament and the amount effective in lowering the work function. Since in the experiments reported in the present paper the emission obtained from the filament was used as the criterion of θ according to Langmuir's relation that $\log i \propto \theta$, there is no contradiction and θ might more properly be defined as the fraction of the tungsten covered with thorium atoms which are effective in lowering the work function.

Becker and Mueller[5] reported that partially activated thoriated and caesiated tungsten surfaces obeyed Schottky's relation,

$$\log i = \log i_0 + \frac{K}{T}\left(\frac{dV}{dx}\right)^{1/2}$$

at high electric fields, but deviated from this as zero potential was approached. They discussed the nature of the fields to be expected close to non-homogeneous surfaces and concluded that poor saturation was to be expected from partially activated cathodes. This effect has been known for some time, but as a subject of detailed study it has been neglected. Dushman[6] and others in their calculations of the electron emission from composite surfaces have projected the $\log i$ vs. $(F)^{1/2}$ line from high fields to zero potential and assumed this as the current emitted at zero field. Since this extrapolated value was several times greater than the current actually obtained, some doubt was thrown on the procedure and it was thought important to investigate in detail the relation between electron current and anode voltage so as to obtain some sort of an explanation of the departures at low fields and perhaps a work-

[3] I. Langmuir, Phys. Rev. **22,** 357 (1923); S. Dushman and J. Ewald, Phys. Rev. **29,** 857 (1927).

[4] J. Becker, Phys. Rev. **33,** 1082 (A) (1929).

[5] J. Becker and D. Mueller, Phys. Rev. **31,** 431 (1928).

[6] Dushman and Ewald, Reference 3; K. Kingdon, Phys. Rev. **24,** 510 (1924); Dushman, Dennison and Reynolds, Phys. Rev. **29,** 903 (1927).

ing picture of the surface. The procedure and results will be briefly stated, and the theory and conclusions left for consideration at the end of the paper.

Figure i shows two typical curves obtained at the same temperature with two values of θ, $\theta_A > \theta_B$. It will be observed that above V_1 both curves follow

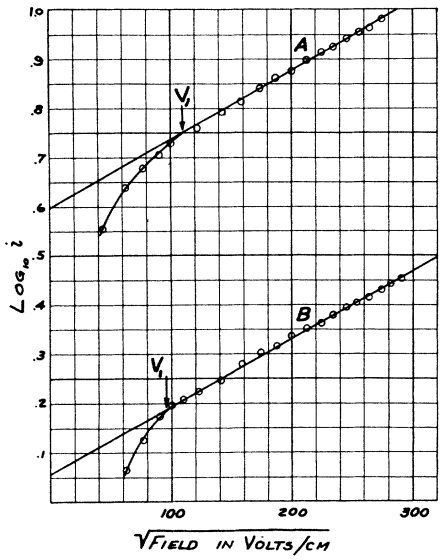

Fig. 1. Typical curves, for two partially activated thoriated filaments, $\theta_A > \theta_B$.

straight lines of approximately the same slope. The theoretical slope can be calculated from the field gradient at the filament surface, as derived from the tube dimensions. The observed slopes varied somewhat, running on the aver-

TABLE I. *From tube geometry,* $T[\Delta \log i/\Delta(V)^{1/2}] = 18.4$.

Run	Temp.	θ	$[\Delta \log i/\Delta(V)^{1/2}]$	$T[\Delta \log i/\Delta(V)^{1/2}]$
28	1045°K	1.0	0.0189	19.77
27	1101	1.0	.0184	20.40
26	1295	1.0	.0138	17.90
87	1350	1.0	.0141	19.05
88	1350	1.0	.0148	19.95
91	1350	0.5	.0150	20.25
101	1350	1.0	.0146	19.70
102	1350	1.0	.0150	20.25
116	1350	0.9	.0143	19.30
107	1375	0.9	.0136	18.70
108	1375	0.9	.0142	19.52
92	1450	0.8	.0145	21.02
112	1450	1.0	.0141	20.45
114	1450	0.9	.0165	23.90
32	1500	0.6	.0127	19.06
			Average	19.93

age about 10 percent higher than the calculated. Table I gives results for various runs at different temperatures and values of θ.

The position of the critical field V_1 must next be considered. This varied slightly from run to run, and the discussion of the effect of positive ion bombardment will show one reason for this variation. However, under the best vacuum conditions, the point of departure from the straight line was constant at about 10000 volts/cm. This appeared to be a limiting minimum value, independent of the temperature and of the state of activation of the filament. So, between $\theta=0.30$ and $\theta=1.0$, and between $T=1100°K$ and $T=1600°K$, Schottky's relation held with very fair accuracy for fields greater than 10000 volts/cm, and this limiting value was characteristic only of the surface thorium on tungsten.

It is interesting to note that in Becker and Mueller's paper, Fig. 5 shows the curve approximating to a Schottky straight line at high voltages but departing from it at about 15000 volts/cm, which is in fair agreement with the results obtained here.

The portion of the curves between V_1 and V_0, the zero of applied potential, presents something of a puzzle. The results vary a great deal, but averaging a large number of runs and eliminating possible complicating factors, there seems to be a certain amount of regularity. Curves A and B of Fig. 1 illustrate this. It will be noted that curve A approaches the dotted straight line more gradually than does curve B. These are two runs at the same temperature, where $\theta_A>\theta_B$. This example and numerous others lead to the generalization that the point of departure, V_1, is approximately independent of θ, but as θ is decreased, the curve falls away more and more steeply. So far, attempts exactly to analyze this portion of the data have failed, yielding only this observed qualitative result.

Removal of liquid air from around the tube resulted in the liberation of small amounts of gas. Thoriated tungsten surfaces are very sensitive indicators of the presence of the least traces of even chemically inert gases, since positive ions produced by electron impacts are accelerated to the filament and remove thorium, reducing θ and consequently the emission obtainable at a given temperature. With "residual gas" ions, this effect becomes important at around 40–50 volts. After such *low voltage bombardment*, the general nature of the log i vs. $(V)^{1/2}$ curves was unchanged, but was shifted vertically downward due to the decrease in the emission current. However, if *bombardment at* 400 *volts or higher* was maintained for a considerable period of time (15-60 minutes), subsequent log i vs. $(V)^{1/2}$ curves in good vacuum exhibited marked changes.

Figure 2 illustrates this. Curve A is a normally activated filament. Curve B was taken after positive ion bombardment at 400 volts. The filament was then flashed at 2800°K and reactivated and curve C taken. This last has been shifted downward in the figure for purposes of spacing. Actually the upper parts of B and C practically coincide, while at low voltages the currents of C are considerably higher than those of B.

The effect of bombardment was a semi-permanent one. Subsequent activation and deactivation by temperature (below 2700°) shifted the curve along the current axis but did not otherwise alter its unique character. Flashing at

2700°K or higher, where rapid sintering of tungsten is known to take place, destroyed the effect of bombardment and subsequent activation produced normal log i vs. $(V)^{1/2}$ curves.

When gas was present in the tube and a run was made, first with ascending and then descending voltages, bombardment occurred while readings were being taken and the curve would not retrace its original path. When the maximum potential used was 1000 volts or higher, the return curve was actually higher than the ascending one, but broke away sooner and crossed the first. A second ascending curve retraced the previous descending one, returning still higher and giving a second sort of hysteresis loop. Thus a filament which at low fields gave higher emission currents than a bombarded one which

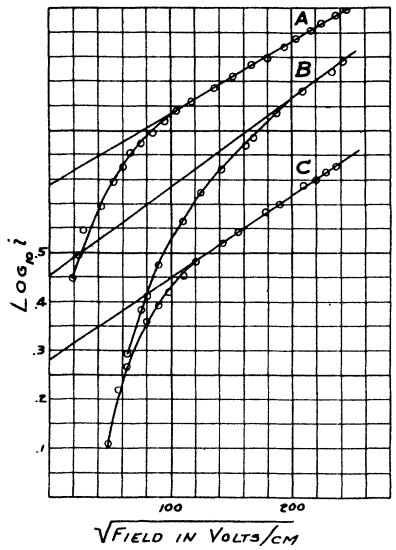

Fig. 2. Curves illustrating effect of positive ion bombardment at 400 volts. Curve A, normally activated filament; B, after bombardment; C, after reactivation. Curve C is shifted downward from practical coincidence with A.

had less thorium present, actually produced less current than the bombarded filament when fields of the order of hundreds of thousands of volts per centimeter were applied. The indication was that something other than the amount of thorium present determined the emission.

A study of the diffusion characteristics of the bombarded filament throws some light on this behavior. Subsequent to severe bombardment, diffusion of thorium to the surface of the wire from the interior occurred at temperatures much lower than in normal thoriated tungsten filaments. The activation rate at 1800°K was about that expected in a normal wire at 2100°K. It is known that diffusion of thorium in tungsten occurs most readily in fine grain structures, presumably along the crystal boundaries. An explanation suggests itself, that the effect of the bombarding positive ions may have been to rup-

ture the surface of the tungsten, producing a superficial fine crystal structure which facilitated the diffusion of thorium atoms. If this had also produced some sub-microscopic roughening, there would have been points where the field strength would have been greatly increased. This would account for a more rapid increase of the current with applied voltage, and an apparent, but not an actual deviation from Schottky's relation.

It was not possible during the course of this investigation to repeat these experiments with a pure tungsten filament and verify this hypothesis, free from the complicating influence of the thorium. However, Bartlett[7] has reported similar results with pure tungsten, giving curves resembling those shown here. He reported difficulty in eliminating gas, and stated that his procedure was to flash the filament and then bombard his anode to red heat to remove gas. Only after this process was he able to obtain satisfactory results. He had only 1000 volts available and was able to go only to about 60000 volts/cm. Up to this point his curves were steeper than the theoretical Schottky line, but were rounding over and approaching this slope. His degassing schedule was an ideal one to produce positive ion bombardment of his filament. It seems possible that the lack of saturation he reports may be the same phenomenon noted here—a roughening of the surface by a positive ion "sand blast"—and that if he had continued to higher fields the curves might have straightened out along the conventional Schottky line. The highest fields used by Bartlett are of about the same order of magnitude as the point of departure of the bombarded curves in the present investigation.

II. Low and Retarding Potentials

If the electrons emitted from a filament at a given temperature all had zero or a constant initial velocity normal to the emitting surface, at a certain anode potential the current should rise abruptly from zero to its full value, and then remain constant, subject to the increase predicted by Schottky's equation, as the potential is increased. It has been shown by several investigators[8] that the emitted electrons have an initial velocity distribution given by Maxwell's equation (via Schottky)

$$i = i_0 \frac{2}{\pi^{1/2}} \left[\left(\frac{Ve}{KT} \right)^{1/2} \epsilon^{-Ve/KT} + \int_{(Ve/KT)^{1/2}}^{\infty} \epsilon^{-x^2} dx \right].$$

Thus, if complicating effects such as voltage drop along the cathode be eliminated, the current should break at a definite potential, and as the anode is made more negative the current should fall away so as to make the log i vs V plot substantially a straight line. The sharp break point defines the absolute zero of potential, i.e., the state at which the anode and cathode are at the same potential, and the difference of this from the zero of applied voltage gives the contact difference of potential (CDP) between the anode and cathode materials. Comparison of two different cathodes or states of surface of the

[7] R. S. Bartlett, Proc. Roy. Soc. **A121**,, 456 (1928).

[8] Davisson and Germer, Phys. Rev. **24**, 666 (1924); Germer, Phys. Rev. **25**, 795 (1925).

cathode with the same anode provides a method of determining changes in the contact potential of a material.

This method was used in examining thoriated tungsten filaments with accelerating and retarding fields in the neighborhood of zero field. Figure 3 shows a typical curve. It will be noted that the left hand portion of the curve follows a straight line, and that after passing through the transition region near zero, the points again approach the nearly straight line saturation value. It was decided to consider the intersection of these two lines, as the experimentally determined zero of potential as a basis for the determination of contact potential differences. This is designated in Fig. 3 as V_c. A justification of this will be given in the discussion to follow.

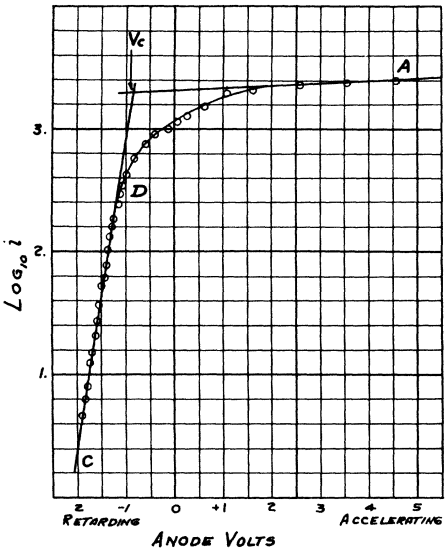

Fig. 3. Typical curve for determining contact potentials.

That part of the straight line just to the left of V_c is a theoretical, not an experimentally obtained curve, since the plotted curve falls away from it before V_c is reached. One cause of this deviation is the voltage drop along the filament cathode. The length of the center anode cylinder of the tube was 2.8 cm, and the difference in the cathode potential opposite the upper and lower ends was considerable and varied with the filament temperature. For this, a first order correction was applied. This was accomplished by first determining the potential of the mid-point of the filament. Then since the current from the most negative end was greater than from the most positive end, and the contribution of each element of the filament did not vary linearly along the filament, a method of graphical integration was used to determine what may be designated as the potential of the effective mid-point of the filament. This is the potential, which applied to a unipotential cathode would give the same observed current. The correction showed that only a part of the devia-

tion near zero could be attributed to the effect of filament drop since, whereas the correction was effective over only a few tenths of a volt range, the observed deviation extended over a range of one or more volts on either side of the determined zero. The effect of the correction on the retarded straight portion of the curve was simply to produce a small lateral shift, altering the actual value of the contact potential break but not the slope of the $(\log i)/V$ line.

Taking this corrected point as zero, and calculating from the filament temperature the fraction of the corresponding saturation current having different initial velocites, a series of points was obtained from Maxwell's distribution law coinciding with the corrected experimental line within the limits of experimental error. Over a 500°C temperature range this effect was verified. At least those electrons with high initial velocities had a Maxwellian velocity distribution. It will be shown later that the apparent deviation of the low velocity electrons (those contributing to the curve near zero voltage) from this distribution was not an actual deviation but was the result of quite another phenomenon.

The low electronic work function of a composite surface, such as thorium on tungsten, has generally been attributed to the effect of the contact difference of potential existing between the thorium and tungsten atoms at their point of contact.[9] Whether the electrons come from the tungsten and are aided in their escape by local fields due to the thorium film, or whether they come from the thorium atoms themselves, it is impossible to state with certainty. Since the currents obtained from the thoriated tungsten are slightly greater than those from a pure thorium filament at the same temperature, and some tens of thousands of times greater than from pure tungsten, it seems reasonable to assume that the emission is that from thorium, modified by the proximity of the tungsten base.

Dushman's[10] derivation of the thermionic emission equation leads to the result:

$$i_0 = A T^2 \epsilon^{-b_0/T}$$

where $b_0 = (e\phi_0/K)$, or $\phi_0 = (K/eb_0)$, and ϕ_0 is the work function of the surface at the abolute zero of temperature. From this equation, it is seen that the value of ϕ_0 for any condition of cathode surface can be found from the slope of the line obtained by plotting $(\log i - 2 \log T)$ against $1/T$. This value of ϕ_0 varies with the amount of thorium present on the surface, ranging from 4.5 volts ($b_0 = 52400$) for pure tungsten, to 2.6 volts ($b_0 = 30500$) for a completely activated filament.

In a preceding paragraph it was pointed out that the difference of the abscissa coordinate V_c from the zero of applied potential V_0 gave a measure of the contact difference of potential between cathode and anode materials. By measuring this difference for different values of θ, to each of which corresponded a definite value of ϕ_0 obtained as just described, a relation was arrived

[9] O. W. Richardson, Phil. Mag. **43**, 557 (1922).
[10] Dushman, Phys. Rev. **21**, 623 (1923).

at connecting the change in contact potential with the change in ϕ_0 for a range of surface conditions. Measurements of the C.D.P. were also made over as wide a range of temperatures as the measuring instruments and other limiting conditions allowed. Since the C.D.P. should be related to ϕ, the work function at the temperature of measurement, while ϕ_0 should be a constant independent of temperature, and presumably

$$\phi = \phi_0 + \pi(T),$$

a study of the change of the C.D.P. with temperature should give an insight into the nature of the function $\pi(T)$. Results are tabulated in Table II.

TABLE II. *Results showing variation of ϕ with temperature.*

I	II	III	IV	V	VI	VII	VIII
			Observed		Corrected	Deviation	Deviation
Run	Temp.	ϕ_ϕ	π_θ	π_1	π_θ	(IV–VI)	%(IV–VI)
57	1175°K	2.85 v	(−)0.3 v	0.08 v	0.30 v	0	0
73	1175	2.73	.4	.30	.18	−.22	—
75	1175	2.68	.3	.28	.10	−.20	—
78	1295	2.68	.3	.28	.36	−.06	16.7
66	1320	3.14	.9	.39	.90	0	0
56	1350	2.85	.5	.28	.68	−.18	26.5
61	1350	2.74	.6	.49	.57	−.03	5.3
59	1350	3.18	1.1	.55	1.01	−.09	8.9
76	1350	2.66	.6	.57	.49	−.11	22.5
84	1375	3.60	1.4	.43	1.48	−.08	5.4
86	1400	2.70	.6	.53	.64	−.04	6.2
63	1450	3.58	1.6	.65	1.62	−.02	1.2
83	1475	3.60	1.7	.73	1.70	0	0
72	1500	2.84	1.1	.89	.99	−.11	11.1
77	1500	2.65	.7	.68	.80	−.10	12.5
68	1550	3.79	2.1	.94	2.05	−.05	2.4
82	1575	3.60	2.0	1.03	1.91	−.09	4.7
64	1660	3.58	1.9	.95	2.07	−.12	5.8
70	1755	3.79	2.4	1.24	2.48	−.08	3.2
						Average	−7.8%

Column III gives the value of ϕ_0 for different values of θ as obtained from the emission data. Column IV lists the contact potential differences from the measurements with retarding fields. These are denoted by π_θ, since they represent results for varying values of θ. Let ϕ_1 denote the value of ϕ_0 for $\theta = 1$ and ϕ_θ for any given value of θ; π_1 and π_θ the corresponding C.D.P. values. Then it is assumed that $\Delta\pi_\theta = \pi_\theta - \pi_1 = \Delta\phi_\theta = \phi_\theta - \phi_1$. Hence $\pi_1 = \pi_\theta - \Delta\phi_\theta$.

Thus, from the observed values of π_θ, an averaged plot of π_1 was obtained as a function of the temperature. These values of π_1 are given in column V. This smoothed curve was used to give corrected values of π_θ, from the observed $\Delta\phi_\theta$. Column VI shows these corrected results, for comparison with the originally observed values of C.D.P. (π_θ). The best justification for this process is the agreement between columns IV and VI. The last two columns give the actual and percentage deviations of IV and VI. In VIII, those cases have been omitted for which the values of $(\pi_\theta - \Delta\phi_\theta)$ were of the order of magnitude of the probable errors of measurement.

In most cases in the experiments, the measurements with retarding fields were made at 0.05 volt intervals throughout the critical range. However, due to the approximation in the correction for filament drop, no claim is made to an accuracy of better than 0.1 volt. The actual magnitude of the measured C.D.P. between the filament and nickel anode can have very little significance. The nickel was at all times positive to the filament. It was noted that after long operation it was impossible to reproduce the earlier readings, an effect traceable to evaporation of thorium to the anode and a consequent shift in the potential of the nickel surface.

The foregoing calculations were based on the assumption that $\Delta\phi_\theta = \Delta\pi_\theta$, and the reasonably close agreement resulting seems to justify this assumption. This seems to be a direct experimental support of Richardson's theory of the essential identity of contact difference of potential and difference of work functions. From this viewpoint, the data of column V are of considerable qualitative interest. They may be interpreted as giving the temperature coefficient of ϕ.

Previous investigators have failed to show conclusively that the work function changes with the temperature. Germer[11] obtained what appeared to be evidence for such a change, but later attributed it to temperature effects inherent in the anode. Whatever the effect in pure metals—tungsten, platinum, and the like—it is small, and the conclusion reached is that the electrons which produce the thermionic current do not share in the temperaure equilibrium in the metal. If they did have a share in the specific heat of the solid they should, by the equipartition theory, contribute an amount at most of the order of $2kT$, an effect barely detectable in these experiments. The results obtained here indicate a temperature coefficient of ϕ of the order of 2×10^{-3} volts per degree, or in the neighborhood of $20kT$. To attribute this to degrees of freedom is obviously absurd.

The constancy of ϕ_0 in the emission equation is not to be doubted, and the method by which the work function is here determined precludes obtaining the value of ϕ and analyzing it for temperature dependence. DuBridge[12] has pointed out that since, for composite surfaces, A in the equation is not constant, and ϕ_0 is by definition a constant, any temperature coefficient of ϕ will be concealed in A. No effort has been made as yet to study the mutual dependence of A and ϕ in a quantitative way.

III. Theoretical Treatment

Langmuir and also Richardson and Young[13] have considered a patch surface to account for lack of saturation of electronic and photoelectric currents fom thin electropositive films. Becker and Mueller[14], in their paper on thoriated and caesiated filaments, calculated that at non-homogeneous surfaces the fields between the two types of atoms should produce the observed depar-

[11] Germer, Reference 8.

[12] DuBridge, Proc. Nat. Acad. Sci. **14,** 788 (1928).

[13] Langmuir, General Electric Rev. 504 (1920); Young, Proc. Roy. Soc. **A104,** 611 (1923).

[14] Becker and Mueller, Reference 5.

tures from Schottky's plot at low applied fields. While any concrete representation of phenomena of atomic behavior may be questioned, the following considerations apparently do offer a tentative explanation of the effects set forth in the foregoing sections of this paper. These considerations were suggested by Dr. K. T. Compton in discussing the interpretation of the present work. It was learned later that the same idea had been carried to a partial quantitative stage a number of years ago by Langmuir and Mott-Smith, but not published.

The work function of a surface is the work required to remove an electron from the surface to infinity. The Thomson method of images furnishes a way of calculating this work, which can be expressed to a first approximation as

$$\phi = -\int_0^\infty (e^2/4x^2)dx.$$

But this leads to an infinite value for ϕ. This difficulty is overcome by assuming that within some small distance x_0 some other law applies, while beyond it the relation given above holds good. Langmuir[15] has shown that whether the force betweeen the surface and x_0 be assumed to be constant or to increase parabolically from zero, the result is the same and the work to reach x_0 is $W = e^2/4x_0$ and then

$$\phi = \frac{e^2}{4x_0} + \frac{e^2}{4x_0} = \frac{e^2}{2x_0}$$

A simple calculation will show that the work required to remove an electron to a distance $10\,x_0$ is 19/20 that needed to remove it to infinity. Thus the factors operating in this region close to the surface are the ones most effective in modifying the work function of the metal and the emission of electrons.

For a perfectly smooth, homogeneous surface, the electric field is constant at any distance outside it, and the work function is constant over it. If, instead of the surface being homogeneous, it consisted of single, isolated atoms of one metal distributed regularly over the surface of the foundation metal, the electric field at atomic distances would be disturbed by the effect of the contact potential between the two metals. However, at a distance of several atomic diameters the field would be very nearly uniform and consequently ϕ would be nearly constant for the whole surface.

The third possible distribution capable of any sort of study would consist of patches of the electropositive material distributed at random over the surface of the other. If such a patch consisted of many hundreds of atoms, it would appear to an electron at a distance $10\,x_0$ normally out from the center of the patch as an infinite plane, and the field acting on the electron, and consequently the work function as applied to that electron would be a perfectly definite magnitude, characteristic of the patch material. Between the patch and the basic metal there would be a potential difference equal to the

[15] Langmuir, Trans. Am. Electrochem. Soc. **29**, 125 (1916).

C.D.P. between the two metals. Let Fig. 4-I represent such a surface. The shaded portions are patches of thorium and the adjacent areas tungsten.

Between these two there is a potential difference of about two volts (assumed since ϕ_0 for full activation is 2.6 volts and for clean tungsten is 4.5 volts). There will be lines of force originating on the thorium, as shown on the diagram. The effect of the fields of force will be to aid electrons to escape from the tungsten but to hinder their escape from the the thorium. Since we assume the electrons under consideration to come exclusively from the thorium, the first effect can be ignored. The retarding action will be more pronounced near the edge of the thorium areas, falling off rapidly as we move toward the center of the patch, and becoming fairly constant and negligible over the central portion.

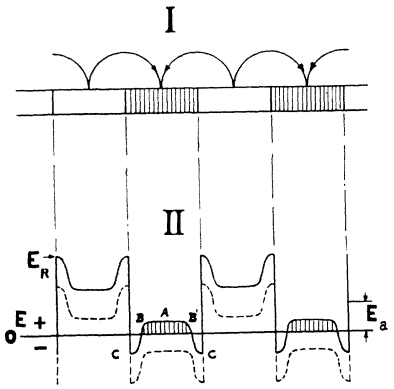

Fig. 4.

Let the dotted line of Curve II–Fig. 4 represent the field resulting from the C.P.D. between thorium and tungsten. The exact shape of the field distribution is indeterminate, but the one shown should be approximately correct. Assume for the present the electrons all to have zero initial velocities. If an external field E_a be applied, the combined effect of this and the "patch field" will be that of the solid line (Fig. 4–II). The shaded area represents the portion of the field accelerating electrons away from the surface. The length defined by it along the abscissa axis represents the part of the thorium covered surface from which electrons can escape from the surface under the influence of the applied field E_a. As E_a is increased from zero, emission begins as soon as the heavy solid line appears above the E_0 axis. Since the center portion of this curve is shown as flat, the area from which electrons can escape increases first rapidly with the voltage, then more and more slowly until finally the whole of the resultant field is in the direction to accelerate electrons away from the metal. At this point, the whole area of the thorium patch is an effective emitter, and the applied field is just strong enough to overcome the maximum field between thorium and tungsten at the point of contact of the two areas. This critical field is independent of the fraction of the surface covered with thorium so long as there remain exposed lines of contact of the two metals.

It should be characteristic only of the C.D.P. between the two metals concerned, and should vary for different pairs of elements.

If now the electrons be assumed to have a Maxwellian distribution of velocities, characteristic of the temperature, investigation with retarding fields should show a perfectly normal distribution curve for the portion BAB' and since we have assumed this line nearly flat, falling off sharply at B and B', the distorting effect of the patch field should be a minimum. As zero is approached and the shoulder of the curve BC begins to emit, the Maxwellian curve will be distorted by the increasing effective area of the thorium brought into action.

Application of this analysis to the typical curve of Fig. 3 shows agreement of the postulated theory and the experimental result throughout the length of the curve. Retarding fields show a Maxwellian distribution. In the neighborhood of zero potential a saturation current is reached, modified by the neutralization of the patch field by the applied field and by the Schottky effect. The patch effect is less and less important with increasing fields until at the point. V_1 (Fig. 1) the whole patch area emits and above this there is saturation emission, increased by the Schottky correction. It will be evident that for some distance above V_1 Schottky's relation will apply only approximately, as the field effective in reducing the surface work function is the difference between the field applied and the field due to the proximity of the tungsten, which is non-uniform over the area of the thorium patch. At very high applied voltages, where the patch field becomes negligible, Schottky's equation should represent the results with very satisfactory accuracy.

The choice of the point V_c as the zero of potential in the contact potential curve (Fig. 3) may need some justification. The point D, lying as it does on the actual curve, would seem at least an equally appropriate reference point, since only *changes* in contact potential are involved. However, the accuracy with which it can be determined is much less. Moreover, this point is modified by the velocity distribution of electrons and is therefore dependent on the temperature. Its sharpness of definition depends upon the shape of the shoulder of the curve E_R (Fig. 4-II). The extrapolated intersection at V_c is much less open to these objections. Also, due to the steepness of the slope of the portion $C\ D$ (Fig. 3) and the flatness of $A\ V$, the uncertainty in the line $A\ V$ due to its actual curvature introduces only a slight error in the determination of the hypothetical zero of potential at V_c.

It is important to note that the necessity of assuming a patch field even for a fully activated surface leads to the conclusion that the tungsten is never fully covered, but that there exist a maximum number of thorium areas distributed over the surface. If the break at V_1 (Fig. 1) is a constant for thorium on tungsten and this field is equal to the maximum retarding field exerted on electrons at the edge of the thorium areas by the tungsten atoms, this field should be of the order of magnitude of the C.D.P. (circa 2 volts) divided by some length which is of the same magnitude as that of the patches. For any different combination of elements, this critical field V_1 should have a different constant value. Thus for caesium on tungsten it should be larger, presumably in proportion to the larger contact difference in potential.

On the basis of this theory there seems to be a real significance to Dushman's extrapolation of the Schottky line to zero field to obtain i_0. This represents the emission from the actual area of electropositive metal present, free from the effects of both the "patch field" and the applied field, and is characteristic of the work function of the surface under consideration.

I take pleasure in acknowledging my indebtedness to the Charles A. Coffin Foundation, since most of the present investigation was carried out while holding one of its Fellowships at Princeton University. Also I tender sincere thanks to Professor K. T. Compton, under whose direction this research was conducted, and whose contributions were many and invaluable; to Dr. S. Dushman, of the General Electric Research Laboratories, for suggestions and criticism; to others in the Laboratories of that company for assistance in preparing apparatus; and to Mr. Robert W. Graves for aid and collaboration during part of the work.

Note added with proof: Since sending this paper to the publisher, these results have been discussed with Dr. Langmuir who has extended his calculations on the properties of a patch surface and reaches conclusions which are in complete disagreement with the observed facts on the Schottky effect. The explanation of this inconsistency between the theoretical deductions and the observations is to be included in a joint report in preparation by Dr. Langmuir and Professor Compton to be published in a forthcoming number of the Physical Review Supplement.