Evidence of a Periodic Deviation from the Schottky Line. I

R. L. E. SEIFERT* AND T. E. PHIPPS
Department of Chemistry, University of Illinois, Urbana, Illinois

(Received June 19, 1939)

A periodic deviation from the Schottky line has been observed for tungsten and for tantalum. For fields less than 4×10^4 volts cm^{-1} the deviations are of the order of the experimental error. For fields greater than this the sign and magnitude of the peak deviations may be seen from the following series, the first number in each case being the value of $E^{\frac{1}{2}}$ in volt$^{\frac{1}{2}}$ cm$^{-\frac{1}{2}}$, and the second being the percent deviation from a least-squares reference line: 200, $+0.03(\pm0.01)$; 265, $-0.07(\pm0.01)$; 365, $+0.12(\pm0.01)$; 501, $-0.11(\pm0.01)$. The data refer to a 1-mil tungsten wire at 1610°K. There is no appreciable effect of temperature upon the positions of the peaks along the $E^{\frac{1}{2}}$ axis. The magnitude of the deviations decreases with increasing temperature. The results with tantalum agree within experimental error with those for tungsten.

INTRODUCTION

SINCE the formulation by Schottky[1] of a theory to account for the increase in the electron current from a hot metal with increase in the accelerating electric field at its surface, numerous investigations[2–11] of thermionic emission have been made to test this theory,[12] which predicts that for all metals

$$\frac{d\log_{10} i}{dE^{\frac{1}{2}}}=\frac{\epsilon^{\frac{3}{2}}}{2.3026k}\frac{1}{T},$$

in which i is the specific electronic current at T°K; E is the accelerating field; ϵ is the electronic charge; and k is Boltzmann's constant. If the unit of E is int. volt cm^{-1}, and if ϵ and k are taken, respectively, as 4.774×10^{-10} e.s. unit and 1.3709×10^{-16} erg deg.$^{-1}$, the coefficient of $1/T$ is 1.908. The results of the earlier investigations deviated from this theoretical slope by as much as 25 to 100 percent. These deviations were attributed in part to uncertainty in the determination of the effective field at the surface of the emitting metal. The more recent investigations by de Bruyne,[7] by Pforte,[9] and by Nottingham[11] have yielded emission curves having slopes which agree within one percent with the theoretical value.

Schottky lines obtained in this laboratory by Phipps and Clemans,[13] with accelerating fields up to 5×10^4 volts cm^{-1}, showed close agreement with the expected Schottky slope, but indicated a perceptible curvature of the line in the sense of a slight decrease in slope with increasing field. This deviation was reproducible and beyond experimental error. The present work sought to increase the accuracy of the measurements and to follow the course of the deviation to higher fields.

EXPERIMENTAL

In order to obtain accurate measurements of the thermionic emission from metals, it is essential that the geometry of the emission tube be known with exactness; that the temperature of the emitting metal be known and kept constant for each isotherm; that the various voltages applied to the collector be accurately known; that the resulting emission currents be accurately measured; and that all the measurements be made in a vacuum sufficiently high that the surface of the metal remain clean and the emission be reproducible during the course of a series of measurements.

* Present address: Alma College, Alma, Michigan.

[1] W. Schottky, Physik. Zeits. **15**, 872 (1914); Ann. d. Physik **44**, 1011 (1914).

[2] W. Schottky, Physik. Zeits. **20**, 220 (1919); Zeits. f. Physik **14**, 63 (1923).

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

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

[5] C. C. Lauritsen and S. S. Mackeown, Phys. Rev. **32**, 326 (1928).

[6] L. A. Dubridge, Phys. Rev. **32**, 961 (1928).

[7] N. A. de Bruyne, Proc. Roy. Soc. **A120**, 423 (1928).

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

[9] W. S. Pforte, Zeits. f. Physik **49**, 46 (1928).

[10] N. B. Reynolds, Phys. Rev. **35**, 158 (1930).

[11] W. B. Nottingham, Phys. Rev. **47**, 806 (1935); **49**, 78 (1936).

[12] For full discussions of this theory see K. T. Compton and I. Langmuir, Rev. Mod. Phys. **2**, 123 (1930); J. A. Becker, *ibid.* **7**, 95 (1935).

[13] T. E. Phipps and J. E. Clemens, unpublished data, 1935.

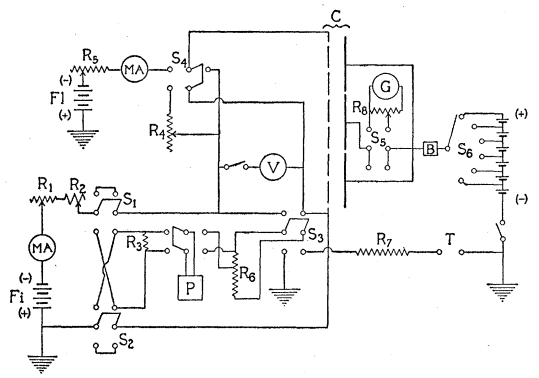

FIG. 1. Electrical circuit. *B*, relay circuit breaker; *C*, thermionic tube; *G*, galvanometer; *MA*, milliammeter; *P*, type *K L* and *N* potentiometer; *T*, terminals for calibration of voltage taps on S_6; *V*, voltmeter.

The thermionic tube

Each of the thermionic tubes, shown diagrammatically in Fig. 1, was constructed as described by Clemens and Phipps.[14] The collecting plates of some of the tubes were formed by the evaporation of platinum onto the walls of the tube, those of others by the evaporation of tungsten. The length (2 to 3 cm) and the diameter (3 cm) of the plates were measured within 0.03 percent at room temperature and corrected to liquid-air temperature. The space between the plate and the guard rings, which never exceeded 0.015 cm, was measured within one percent. One-half the width of each of these two spaces was added to the length of the plate. A straight tungsten filament was mounted coaxial with the plate and guard rings, well within 0.05 cm of the exact center. Filaments, 2 mils, 1 mil, and 0.5 mil in diameter, of high purity, cleaned tungsten wire, No. 218, obtained from the Incandescent Lamp Department of the General Electric Company, were used.* The exact diameters of the filaments were obtained by determining the length and weight of one-meter samples taken from each end of the sections which were used for filaments. Each length was measured with an accuracy of 0.01 percent and each weight with an accuracy of 0.05 percent.† The diameter of each sample was then calculated from the relation given by Jones and Langmuir,[15] and the average value for each pair of samples was taken as the diameter of the section from which the samples were obtained. The uniformity of the filament diameter appears to have varied between the different filament sizes, though in no case did the calculated diameters of the two individual samples vary by more than 0.2, 0.08 and 0.06 percent, respectively, for the 2-mil, 1-mil and 0.5-mil filaments. These filament diameters, calculated at room temperature, were corrected to the operating filament temperatures by use of the thermal expansion data given by Jones and Langmuir.[16]

Filament temperature

The temperature of the filament was determined from the current-diameter-temperature data given by Jones and Langmuir.[15] In the calculations presented herein the temperatures given in the table of Jones and Langmuir have been assumed to be correct.[17] The filament current was determined by measuring the potential drop across the one-ohm standard resistance* R_3 (Fig. 1) with the potentiometer *P*. The standard resistance was calibrated within 0.01 percent, and the potentiometer was calibrated by the method of Young and Hartouch[18] to 0.01 millivolt. The standard cell used with the potentiometer was calibrated to six significant figures by the National Bureau of Standards. The resulting accuracy with which the potential drop across the standard resistance was determined at the lowest filament temperature for the 2-mil, 1-mil and 0.5-mil filaments was 0.01, 0.03 and 0.006 percent, respectively. Therefore, the maximum possible error of the filament

[14] J. E. Clemens and T. E. Phipps, Rev. Sci. Inst. **8**, 133 (1937).

* Tungsten wire of still higher purity has recently been furnished us by the Incandescent Lamp Department of the General Electric Company, through the courtesy of Mr. B. L. Benbow. The data in the present paper, however, refer only to the No. 218 wire.

† Mr. C. W. Beazley weighed these samples on a microbalance, using weights calibrated by the National Bureau of Standards.

[15] H. A. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 310 (1927).

[16] H. A. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 354 (1927).

[17] The accuracy of this temperature scale has been questioned by W. H. Brattain and J. A. Becker, Phys. Rev. **43**, 428 (1933); by W. B. Nottingham, *ibid.* **49**, 78 (1936); and by H. B. Wahlin and L. V. Whitney, *ibid.* **50**, 735 (1936).

* A calibrated ten-ohm standard resistance was used with the 0.5-mil filaments.

[18] T. F. Young and P. J. Hartouch, private communication.

temperature resulting from the experimental measurements here involved was less than 0.2 percent even in the most unfavorable case. By the use of a galvanometer of high voltage sensitivity in the potentiometer circuit, it was possible to keep the filament current constant well within 0.003 percent by hand regulation of resistance R_2 (Fig. 1). In order to facilitate keeping the filament current constant to this degree, switch S_4 and resistance R_4 were introduced so that the filament could be flashed by batteries *Fl* without appreciably disturbing the current flowing from the filament batteries *Fi*. The switches S_1 and S_2 made it possible to introduce the standard resistance at either end of the filament, so that it was possible to keep either the input or output of the filament current constant at the value corresponding to the setting of the potentiometer *P*. For filament temperatures lower than 2000°K the electron emission was the same with the standard resistance in either position. Therefore, at these temperatures no measurable gradient of the heating current along the filament was produced by the emission current.

Plate potentials

The plate potentials, which were applied by means of the mercury switch S_6 (Fig. 1), were obtained from a bank of Burgess Heavy Duty "B" Batteries, the maximum voltage of which was about 2400 volts in the earlier measurements and about 4700 for the later work. In order to avoid drawing currents sufficiently large to produce a noticeable polarization, the batteries were calibrated in steps of less than 140 volts, before and after each series of emission measurements, by means of the potentiometer *P* and the volt box arrangement R_6 and R_7. The total potential of each of the available taps on switch S_6, as obtained by the summation of the constituent steps, varied less than 0.1 percent over a period of several months, when corrected for the temperature coefficient of the battery potential. It was therefore assumed that the e.m.f. of the battery remained constant throughout a series of emission measurements, and that values at the different taps were those given by a recent calibration, except for correction to the existing battery temperature. These applied battery potentials had to be corrected, however, for the voltage drop down the filament; for the drop across the standard resistance, if the latter were on the grounded side of the filament; for the voltage drop across the high resistance protective relay *B* (Fig. 1); and finally for the contact potential between the filament and the plate. The voltage drop down the filament from ground to the center of the plate was easily determined within 0.01 volt from the determination of the filament voltage with the volt box R_6 and the measurement of the corresponding filament sections. The emission current was so small that the voltage drop across the relay *B* was negligible except at the higher filament temperatures. At these temperatures it was calculated from the resistance of the relay and the measurement of the total emission current to plate and guard rings. The contact potential was determined to within 0.1 volt by the method described by Becker.[12]

Measurement of emission current

The emission current was measured by means of a current-sensitive G-M galvanometer, which had been equipped in this laboratory with a quartz fiber suspension of approximately 18μ (0.0018 cm) diameter, in order to produce a better zero return of the galvanometer coil than that obtainable with metal ribbon suspensions. With quartz fiber suspension, even after a full scale deflection of 80 cm at 5 meters' scale distance, the coil consistently returned to within 0.1 mm of the initial zero reading. Calibration proved the galvanometer deflection to be linear with current over the entire scale length, within the possible 0.1 mm error in the reading of the deflection. For each filament temperature the galvanometer sensitivity was adjusted by setting the shunt resistance R_8 (Fig. 1) so that a full scale deflection resulted upon the application of the highest plate voltage. This shunt setting was then used for all measurements at that temperature. Consequently the relative emission currents for each isotherm were given by the galvanometer deflections and were independent of the galvanometer sensitivity determinations. However, the possible error in each galvanometer reading being 0.1 mm, the percent error in the deflections was larger for the lower applied voltages than for the higher, since in the former

case the galvanometer deflections were smaller. In order to obtain the absolute values of the emission currents, the galvanometer was calibrated by means of a White potentiometer. Over a period of several weeks the galvanometer sensitivity thus determined varied within 0.15 percent of the mean value, though the possible experimental error of each calibration was considerably less than this. The galvanometer was introduced into the plate circuit by means of the mercury cup switch S_5 (Fig. 1), which was so constructed that the galvanometer could be introduced without interrupting the plate current. Thus the surge of current from the plate produced by the application of high plate potentials did not pass through the galvanometer to cause a sudden excessive deflection and vitiate the excellent zero return of the coil. The entire plate circuit was so well insulated that no measurable current passed through the galvanometer when the highest plate potential was applied with the filament cold.

Procedure

For the duration of each series of measurements the thermionic tube remained sealed to the vacuum line while the mercury pumps operated continually. Initially the tube and vacuum line back to the first diffusion pump were baked out at 480–500°C for at least 48 hours. Thereafter liquid air was kept constantly about a trap between the tube and the pumps. The thermionic tube was immersed in liquid air during the time that the filament was being aged and emission measurements made. The filament was aged according to the schedule given by Taylor and Langmuir.[19] After the filament was flashed five or six times to give a total of one minute at 2900°K, the emission, contrary to expectation, continued to increase slightly upon further flashing at that temperature. However, calculations, based upon the evaporation data given by Jones and Langmuir,[15] showed that this increase in emission could be accounted for entirely by a rise in filament temperature resulting from the passage of the same current through the filament now slightly thinned by evaporation. After aging the filament, the tube and vacuum line were again baked out as before.

After testing the tube to insure that both guard rings were functioning and that there was adequate insulation between them and the plate, emission measurements were made by maintaining a constant filament temperature and applying to the plate in succession the voltages available on the mercury switch S_6 (Fig. 1). At frequent intervals measurements were repeated at previously employed voltage taps in order to test the reproducibility of the emission. Only occasionally (usually following the application of high voltages) did the galvanometer deflection fail to check within one or two tenths of a millimeter a former reading at the same tap. This was thought to be due to the release of an oxidizing gas from the plate under electron bombardment, and a consequent coating of the filament; for, after flashing the filament to 2400 or 2600°K, it was again possible to check former deflections. Since continued flashing at 2400–2600°K did not change the emission, and since the emission would normally remain constant for more than an hour without further flashing of the filament, it was concluded that the surface of the tungsten was clean and that the residual gases in the vacuum were not influencing the emission.

Discussion of Results

Choice of reference line

Many emission isotherms ($\log_{10} i$ *versus* $E^{\frac{1}{2}}$) were obtained for 2-mil, 1-mil, and 0.5-mil tungsten filaments and for a 2-mil tantalum filament, in a number of different experimental tubes. As has been briefly reported previously,[20] these curves were all similar in that the experimental points deviate in a regular manner from a straight line. In order to show this fluctuation more clearly than is possible on a curve of $\log_{10} i$ against $E^{\frac{1}{2}}$, the deviation of the experimental points from a reference line was plotted against $E^{\frac{1}{2}}$. In each case the reference line was obtained by calculating the most probable straight line through the experimental points by the method of least squares. This procedure for selecting a reference line was quite arbitrary,

[19] J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 430 (1933).

[20] R. L. E. Seifert and T. E. Phipps, Phys. Rev. **53**, 493 (1938).

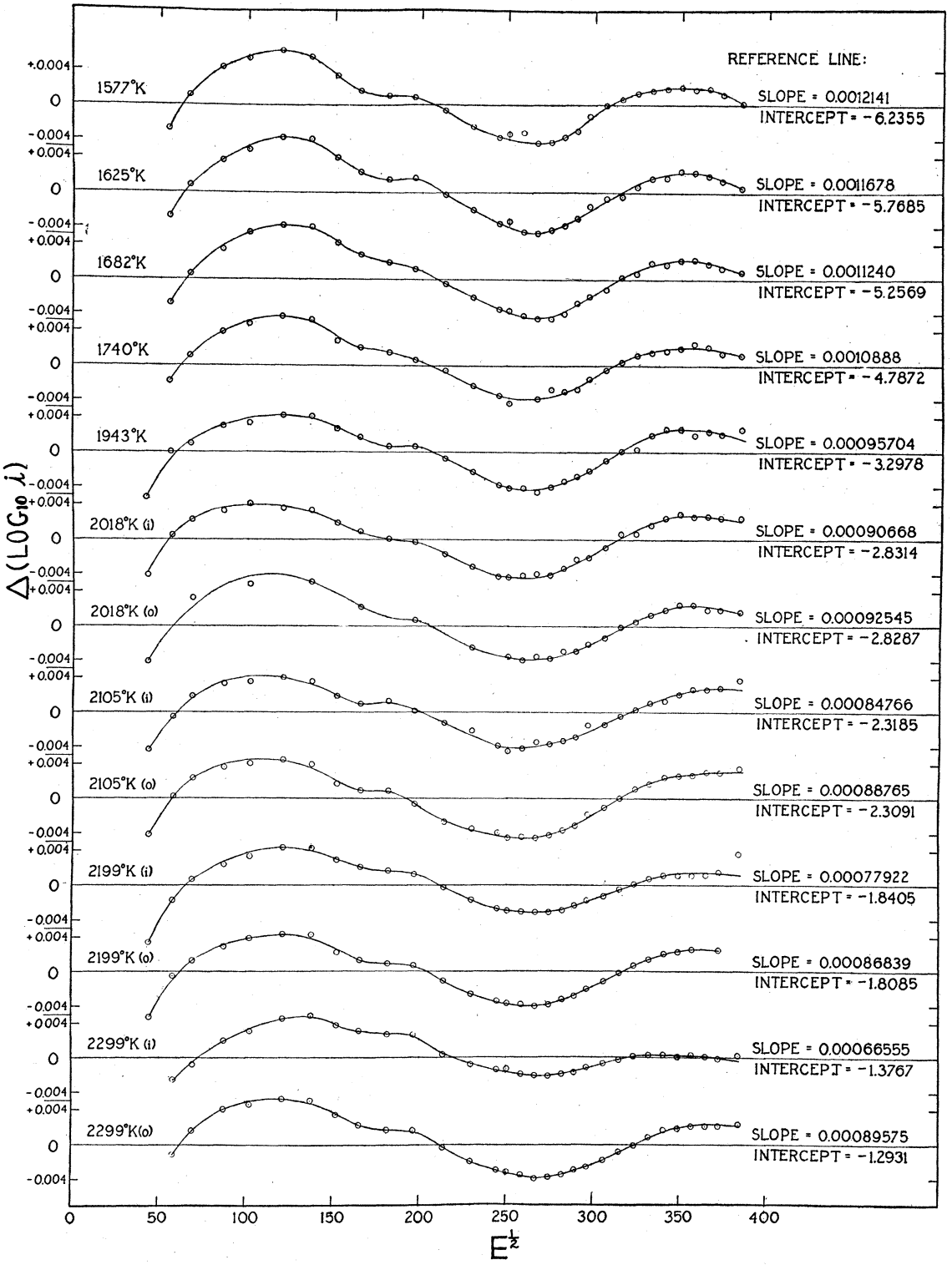

FIG. 2. Δ ($\log_{10} i$), the deviation of the logarithm of the isothermal specific emission current from the reference line indicated, as a function of $E^{\frac{1}{2}}$, the square root of the field (volt$^{\frac{1}{2}}$ cm$^{-\frac{1}{2}}$) at the surface of the emitting tungsten. Data obtained with 2-mil tungsten filament, in thermionic tube 1-D with platinum plates and spiral-spring mounting of filament. The notation T°K(i) indicates that the current input was kept constant at the value calculated for T°K; similarly, T°K(o) designates constant output at the value calculated for T°K. (Only for filament temperatures above 2000°K was the electron emission less for constant input than for constant output.)

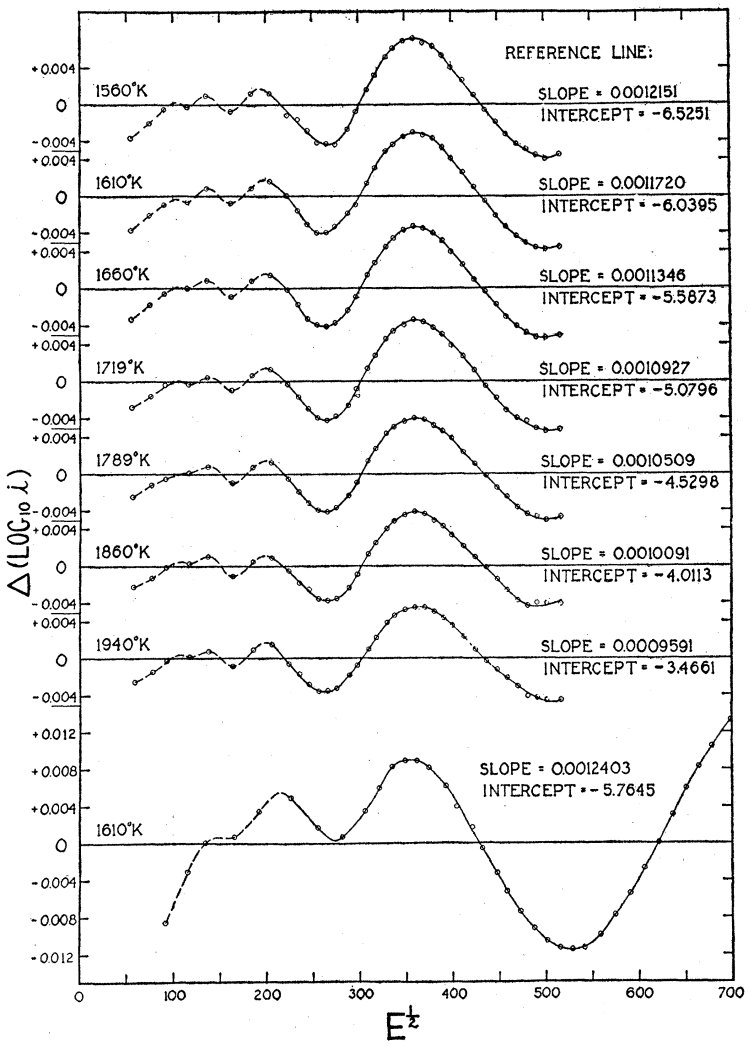

FIG. 3. Δ ($\log_{10} i$), deviation of the logarithm of the isothermal specific emission current from the reference line indicated, as a function of $E^{\frac{1}{2}}$, the square root of the field (volt$^{\frac{1}{2}}$ cm$^{-\frac{1}{2}}$) at the surface of the emitting tungsten. The upper seven curves are for a 1-mil tungsten filament. The lowest curve is for an incompletely aged 0.5-mil tungsten filament. Data were obtained with thermionic tube 2-C, with tungsten plates, and with spiral-spring mounting of filaments.

since any curve obtained by a least-squares calculation has significance only if the displacement of points from the resulting curve arises from random errors. In this case, even a casual inspection of a large-scale plot of $\log_{10} i$ against $E^{\frac{1}{2}}$ revealed that the deviation from a straight line was not random but regular and periodic. Nevertheless a least-squares reference line was employed since its intercept on the axis of ordinate is directly comparable with the "zero field" values of $\log_{10} i$ of earlier experimenters, whose usual practice was to extrapolate a least-squares line to zero field.

The resulting deviation curves for some of the filaments are shown in Figs. 2, 3, 4 and 5, in which the deviation is given in the same units as $\log_{10} i$. The values of slope and intercept given to the right of each curve are those calculated by the method of least squares for the reference line that was used in obtaining the deviation curve. It is seen that the heights of the maxima and minima for a given filament decrease slightly

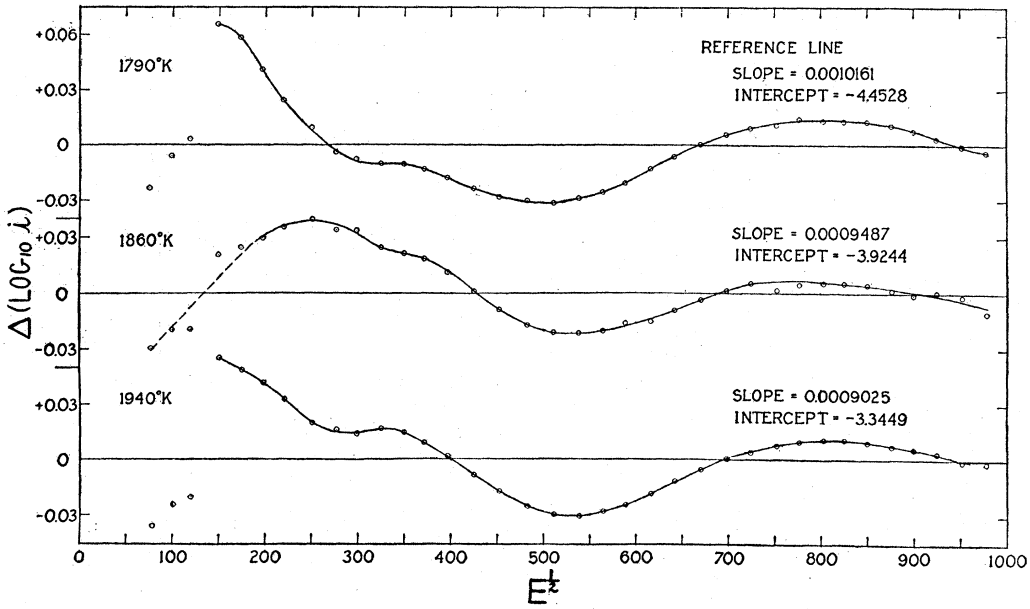

FIG. 4. $\Delta(\log_{10} i)$, deviation of the logarithm of the isothermal specific emission current from the reference line indicated, as a function of $E^{\frac{1}{2}}$, the square root of the field (volt$^{\frac{1}{2}}$ cm$^{-\frac{1}{2}}$) at the surface of the emitting tungsten. Data obtained with a 0.5-mil tungsten filament, in thermionic tube 3-A, with platinum plates, and with loop-spring mounting of filament.

with increasing temperature, as is best shown by the 1-mil data, Fig. 3, which were obtained with tungsten plates. The steadiness of emission and the reproducibility of the data were even better in this case than with the other filaments.

Experience with 0.5-mil wire

The sets of curves shown for the 2-mil (Fig. 2), 1-mil (Fig. 3), and 0.5-mil (Fig. 4) tungsten have been chosen because each set represents a series of isotherms obtained with the same filament and tube. The tungsten plates which were used for obtaining emission data with 1-mil filaments permitted even better vacuum conditions than had been obtained with the platinum plates used with the 2-mil filaments. It was observed, however, that the tungsten plates pitted badly under high voltage electron bombardment. Since a higher range of plate voltages was available at the time when the 0.5-mil data were obtained, platinum plates were again used.

The 0.5-mil filaments, when mounted with spiral springs, invariably burned out before the aging had been completed. The 0.5-mil curve which is included in Fig. 3 was accordingly taken after only a partial aging, namely, after 3 hours at 2400°K. In this case the emission at representative voltage taps was then observed after short intervals of further aging. The following behavior was observed. An additional 7 hours aging at 2400°K decreased the emission to 97.5 percent of the value observed after 3 hours. One hour at 2600°K increased the emission to approximately 100 percent, and also increased the effect of applied voltage upon emission above that which was observed after the initial aging. Thus, after the one hour of aging at 2600°K the emission current at the lowest plate voltage was 0.4 percent less and at the highest plate voltage 0.6 percent greater than it had been after the initial three hours of aging at 2400°K. Despite these confusing results of aging which shifted the position of the emission curve along the $\log_{10} i$ axis, the positions and magnitudes of the deviations from a straight line did not change. The 0.5-mil data shown in Fig. 4 were obtained when using a semi-circular loop spring to mount the filament. This permitted complete aging of the filament without its burning out.

Variation of experimental conditions

In addition to using different plate material in a number of tubes, the following variations were also made. During the course of the work two

different electrical circuits were used, which were mounted in different positions in the laboratory. In these two circuits the instruments were placed in different relative positions, the wiring diagram remaining essentially the same. The "B" batteries were wired in a different order in the two circuits, and voltage taps of different value were used as the total available voltage was increased. The same galvanometer was used in each case; however, the respective scale distances were approximately 8 meters and 5 meters, so that the angular deflection of the galvanometer coil to produce a given reading was different in the two cases. Different sections of the scale were used for making emission measurements over the same range of applied voltages, in order to insure against errors due to non-uniformity of the scale or to its position. These variations in the experimental conditions had no effect upon the deviation curves. This was taken to indicate that the periodic deviations do not arise from experimental defect, but are to be regarded as a property of the emitting surface. Since the deviation curves for aged tantalum (Fig. 5) and for incompletely aged tungsten (bottom curve, Fig. 3) are identical with those of aged tungsten in respect both to position of the deviations along the E axis and to their magnitude, it follows that the effect is independent of both the state and the nature of the metal surface, as is the Schottky effect itself. At considerably higher fields, for which the "characteristic distance" of the Schottky theory is of the order of a few angstrom units only, it cannot be assumed that the periodic deviations will continue to be independent of the nature of the surface.

Variation in the shape of the deviation curves

Similarity between the deviation curves obtained for the different sizes of filaments is obscured somewhat by the fact that the method of least squares is not applicable for obtaining comparable reference lines, since both the slope and the intercept of such lines depend upon the range of field values used and upon the distribution of the experimental points along the $E^{\frac{1}{2}}$ axis. This comes from the fact, already mentioned, that the experimental points do not deviate from a straight line in accordance with a statistical distribution of error, but rather in accordance with the small, though definite, periodic deviation here revealed. The fact that the deviation curves for the 1-mil filaments (Fig. 3) appear to lie fairly symmetrically about the calculated reference line is considered to be the result of a fortuitous termination of the experimental curve at a point which favored symmetry about the least-squares line. Whether or not it is desirable to choose a line of symmetry as reference line will depend upon the theoretical significance to be given to the deviation. A line with the Schottky slope and an empirically adjusted intercept has been employed on

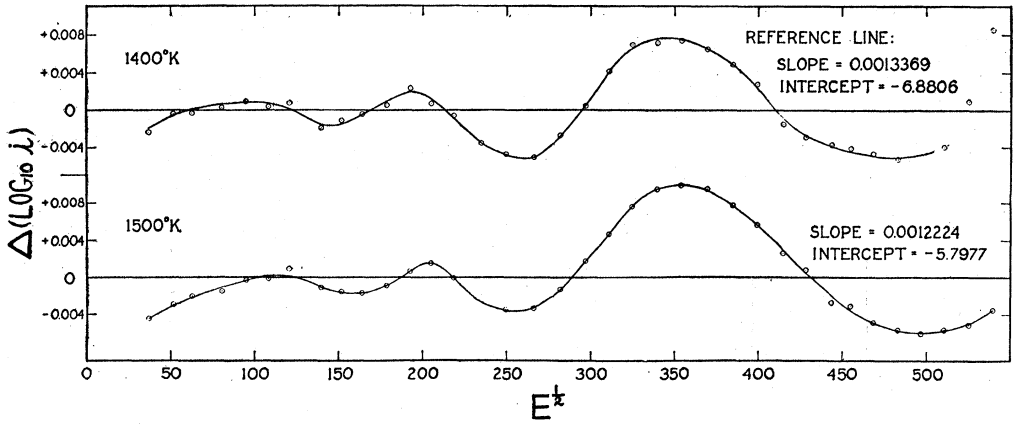

FIG. 5. Δ ($\log_{10} i$), deviation of the logarithm of the isothermal specific emission current from the reference line indicated, as a function of $E^{\frac{1}{2}}$, the square root of the field (volt$^{\frac{1}{2}}$ cm$^{-\frac{1}{2}}$), at the surface of the emitting tantalum. Data were obtained with a 2-mil tantalum filament, in thermionic tube 3-A, with platinum plates, and with spiral-spring mounting of filament.

occasion as a reference line. The deviation curves with respect to such a line were very similar to those in the figures except that the deviations were negative, with the result that the deviation curve showed a downward trend from the horizontal reference line with increasing field. A Schottky line may nevertheless be a line of symmetry, since an ill-chosen value for the electronic charge or an error in temperature inherent in the temperature scale adopted (or both causes together) may have led to an incorrect value for the Schottky slope and consequently to a deviation curve unsymmetrical with respect to a line of that slope.

The calculation of work function

In determining the work function of a metal at zero applied field, use has frequently been made of the emission at zero field as obtained by a linear extrapolation of the $\log_{10} i - E^{\frac{1}{2}}$ line to the axis of ordinate. Since deviations from exact linearity do exist and since these deviations increase in magnitude with increasing field, the resulting value at zero field will depend upon the experimental range of applied field from which the extrapolation is made, as well as upon the distribution of the experimental points within the range of field under consideration. Thus, for example, if the work function, ϕ, of tungsten is calculated from the Richardson equation, $i_0 = AT^2 \exp[-\varphi\epsilon/kT]$, using the values of zero field emission found by linear extrapolation of a least-squares line involving all points of the isotherms shown in Fig. 2, the resulting value of ϕ is different from that obtained if only a portion of the experimental data is used in the calculation of $\log_{10} i$. Table I gives the slope and intercept of each of the least-squares straight lines obtained for the entire 1577°K isotherm and for two segments of it. The values of ϕ given in Table I

TABLE I. *Thermionic emission data for tungsten.*

Range of field, volt cm^{-1}	2500 to 150,000	70,000 to 115,000	115,000 to 150,000
Slope of isotherm, 1577°K	0.0012141	0.0013201	0.0011609
Intercept of 1577°K isotherm	−6.2355	−6.2702	−6.2161
Work function, electron volt	4.556	4.567	4.539

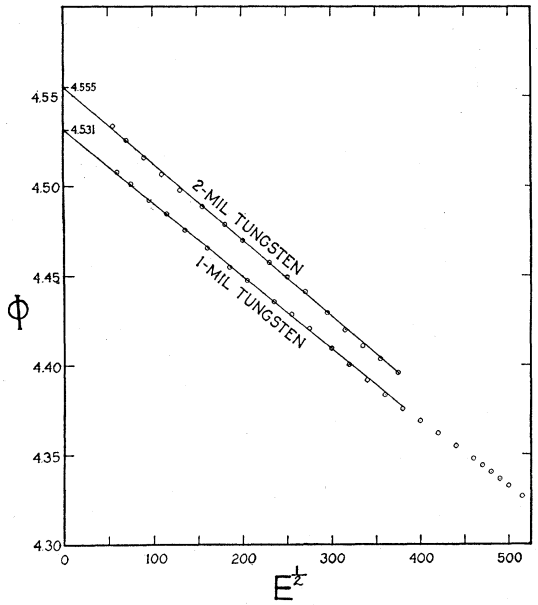

FIG. 6. The work function ϕ (electron volt) of tungsten as a function of $E^{\frac{1}{2}}$, the square root of the field (volt$^{\frac{1}{2}}$ cm$^{-\frac{1}{2}}$) at the surface of the tungsten.

are calculated* from the values of i_0 obtained by extrapolation of the other isotherms in Fig. 2 over the same ranges of applied field. If ϕ is calculated from data taken throughout a still higher range of applied fields, the results may be expected to vary by even a larger amount owing to the larger deviations from the Schottky line at higher fields.

Discussion of errors

From the smoothed deviation curves it is possible to calculate the actual emission at the same applied field for all filament temperatures, and therefrom to obtain the values of ϕ and A at that applied field for the filament under consideration. The resulting values of ϕ and A as a function of $E^{\frac{1}{2}}$ are shown in Figs. 6 and 7 for the 2-mil and 1-mil data of Figs. 2 and 3. These values of ϕ and A for each value of $E^{\frac{1}{2}}$ were calculated from the slope and intercept of the least-squares straight line through the points on a Richardson plot for that value of $E^{\frac{1}{2}}$. From the residuals of the ordinates it was possible to

* In the calculation of the values of ϕ given in this paper the charge on the electron was taken as 4.774×10^{-10} e.s.u. For filament temperatures above 2000°K use was made of the average value of $\log_{10} i$ as obtained from the two curves, one for constant filament input and the other for constant output. (See legend under Fig. 2.)

calculate the probable error in each of the values of ϕ and A. The maximum values found for the probable errors of ϕ and A, considering all values of $E^{\frac{1}{2}}$, were 0.0029 e.v. and 1.01 amp. cm^{-2} deg.$^{-2}$, respectively. The probable errors calculated for most of the points shown were considerably less than this. These calculated probable errors take account of experimental errors in the determination of the galvanometer sensitivity at each shunt value, and also of experimental errors in the determination of the "Jones-Langmuir temperature"; but they do not take account of inherent errors in the determination of the absolute magnitude of either quantity. For this reason the actual uncertainty in the values of ϕ and A is much greater than would be indicated by the small probable errors, though this additional error is the same for all the values of ϕ and A.

In addition to the errors just mentioned there is another source of error in the determination of the filament temperature; namely, that the filament is mounted at the center of a reflecting metallic plate held at the temperature of liquid air, whereas the current-diameter-temperature function[15] was determined with the filament surrounded by clear glass walls at room temperature. To determine the order of magnitude of the error thus introduced, measurements were made of the potential drop across the central 2-cm section of a 12-cm length of 2-mil tungsten filament, both when mounted at the center of a tungstenized glass tube and when mounted at the center of a clear glass tube, the filament current being maintained at the same set of values in each case. These measurements were made at seven different filament temperatures in the range 1600–1940°K. When mounted at the center of the tungstenized tube the resistance of the filament was found in each case to be 0.6 ($\pm$0.02) percent greater than when mounted in a clear glass tube. The possible effects of different plates, different sizes of filament, and exact positions of mounting were not determined. This constant error in T would give rise to the same percent error in ϕ and to twice as great a percent error in A. This "plate reflectivity" error in temperature may account for the discrepancy of 0.51 percent in the work function (shown in Fig. 6) between results obtained with platinum and with tungsten plates. Such a constant error in T is not as serious as a variable error would be; for the latter may lead to relatively large errors in ϕ and in A, particularly if the temperature range is short, and the number of filament temperatures employed is small.

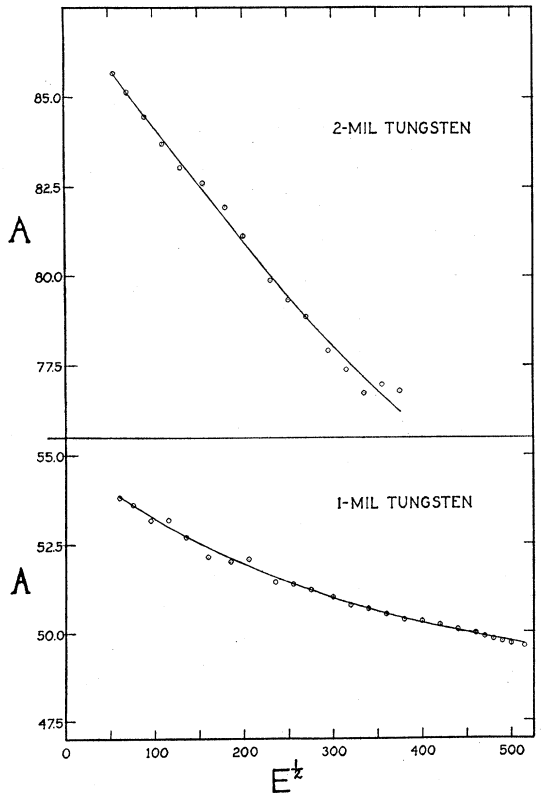

FIG. 7. The Richardson constant A for tungsten as a function of $E^{\frac{1}{2}}$, the square root of the field (volt$^{\frac{1}{2}}$ cm$^{-\frac{1}{2}}$) at the surface of the tungsten.

The effect of field upon work function

While the absolute values of ϕ here calculated are in error due to the causes mentioned above, the percent error is constant in all the values of ϕ on a ϕ *versus* $E^{\frac{1}{2}}$ plot, such as the two shown in Fig. 6. In these curves, then, we may observe the effect of the applied field upon the Richardson work function, ϕ. In Fig. 6 "zero field" work functions have been found by extrapolating the least-squares straight line calculated for the experimental points in the range of $E^{\frac{1}{2}}$ from 60 to 380 volt$^{\frac{1}{2}}$ cm$^{-\frac{1}{2}}$. (In spite of the small scale of the plot in Fig. 6 the periodic deviations from these lines can be observed; these deviations are magnified in Fig. 8.) The slope of the line, ϕ

versus $E^{\frac{1}{2}}$, should be, according to the Schottky theory, $-(299.9\epsilon)^{\frac{1}{2}}$ for the units employed here. The experimental values of the slopes determined from the 2-mil and the 1-mil data, respectively, are -4.246×10^{-4} and -4.073×10^{-4} volt$^{\frac{1}{2}}$ electron cm$^{\frac{1}{2}}$. Even if the recently suggested[21] larger value of ϵ, 4.8029×10^{-10} e.s.u. were used in all the calculations, the theoretical Schottky slope would be only 3.795×10^{-4} volt$^{\frac{1}{2}}$ electron cm$^{\frac{1}{2}}$, which is 10 percent less than the experimental value would be for the 2-mil data and 6 percent less than that from the 1-mil data. This discrepancy may rise from two obvious sources (other than that which comes from uncertainty in the value of ϵ); namely, from error in the factor converting applied plate voltage to effective field at the surface of the emitter, and from a constant percent error in the absolute values of ϕ.

Deviation curves for ϕ and A

In order to show more clearly the deviations of ϕ from a linear function of $E^{\frac{1}{2}}$, the line in Fig. 6 for the 1-mil filament was extrapolated to the higher fields and the deviations of ϕ from this line were calculated. The resulting deviation curve is shown in Fig. 8. At low fields, because of the increased percent error in $E^{\frac{1}{2}}$, and because of proximity to "space-charge" conditions, the measurements are less accurate than at high fields. Consequently it cannot be said with certainty whether the deviations in this range are nonexistent or are only being masked by the large errors. In this connection it should be pointed out that the deviation curve is sensitive to errors in $E^{\frac{1}{2}}$, since an error in this quantity shifts a point on the deviation curve both horizontally and vertically from its correct position. Since the values of ϕ and A were calculated from the emission as given by the smoothed deviation curves (Figs. 2 and 3), errors in the position of these deviation curves at low fields resulted in errors in both ϕ and A at the same values of $E^{\frac{1}{2}}$.

It can be seen in Fig. 7 that the experimental values of A lie consistently on a smooth curve[22] only at high values of $E^{\frac{1}{2}}$. In order to obtain a magnified deviation curve it is desirable to have as reference line a simple curve which lies near the experimental points. In order to obtain such a deviation curve for the 1-mil data shown in Fig. 7, the equation $A=54.800-0.01700E^{\frac{1}{2}}+1.400\times10^{-5}E$ was used as a reference curve. The resulting deviation curve (Fig. 8) gives slight evidence that the values of A tend to exhibit maxima and minima at the same values of E at which maxima and minima appear in the emission ($\log_{10} i$ *versus* $E^{\frac{1}{2}}$) curves. However, the

[21] R. T. Birge, Nature **137**, 187 (1936).

[22] The slope of the A *versus* $E^{\frac{1}{2}}$ curve, according to the Schottky theory, is zero.

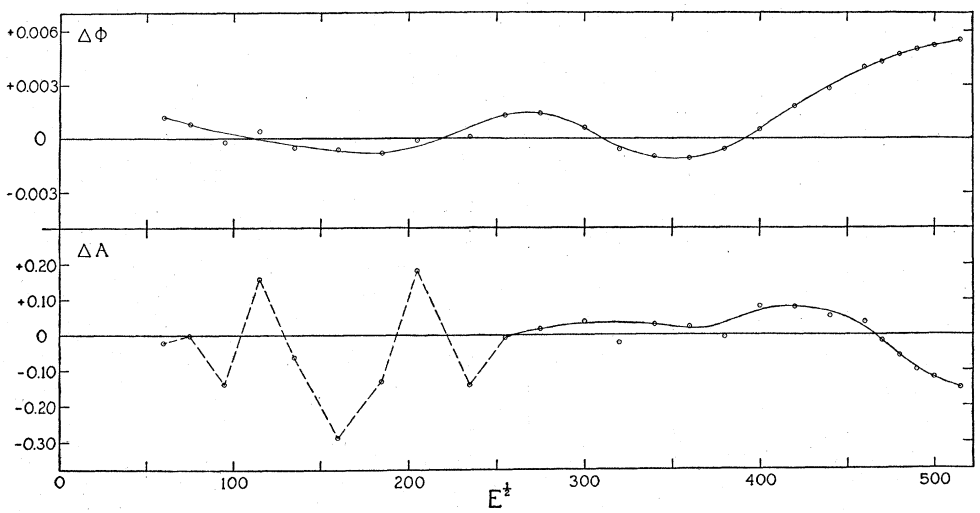

FIG. 8. Top curve: Deviation in electron-volts of ϕ for the 1-mil tungsten (Fig. 6) from the reference line, $\phi=4.531-4.073\times10^{-4}E^{\frac{1}{2}}$. Bottom curve: Deviation in amp. cm^{-2} deg.$^{-2}$ of A for the 1-mil tungsten (Fig. 7) from the reference curve $A=54.800-0.01700E^{\frac{1}{2}}+1.400\times10^{-5}E$.

existence of maxima and minima in the A curve is not as pronounced as in the ϕ curve. The ϕ values show definite maxima and minima at values of $E^{\frac{1}{2}}$ corresponding, respectively, to minima and maxima in the emission curves (compare Figs. 8 and 3). It appears then that the Richardson work function, ϕ, is a periodic function of $E^{\frac{1}{2}}$, which exhibits an increasing amplitude with increasing field. The deviation from a least-squares line is small; the maximum value up to applied fields of the order 250,000 volts cm^{-1} is about 0.1 percent of the value of ϕ. The fact that the Richardson A as well as the Richardson ϕ may be a periodic function of $E^{\frac{1}{2}}$ could be due to the form of the Richardson equation; for, if the work function is not constant, but varies linearly with the temperature, the coefficient of T appears in the experimental constant A.

The periodic deviations from the Schottky line reported above are given theoretical consideration by Dr. H. M. Mott-Smith in an accompanying paper.

OCTOBER 1, 1939 PHYSICAL REVIEW VOLUME 56

Evidence of a Periodic Deviation from the Schottky Line. II

D. TURNBULL AND T. E. PHIPPS
Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

(Received June 19, 1939)

The periodic deviation from the Schottky line observed by Seifert and Phipps was studied in greater detail for tungsten up to fields of 6.5×10^5 volts cm^{-1}. The deviation continued with increasing period and amplitude up to the highest fields investigated. The characteristic Schottky distance from the surface, x_0, was calculated for all values of the field at which maximal and minimal values of the deviation occurred. The difference between successive x_0 values was of the order 24A between $E^{\frac{1}{2}}=160$ and $E^{\frac{1}{2}}=266$; of the order 17A between $E^{\frac{1}{2}}=266$ and $E^{\frac{1}{2}}=505$; and of the order 12A between $E^{\frac{1}{2}}=505$ and $E^{\frac{1}{2}}=752$. The temperature coefficient of the position of these maximal and minimal values along the $E^{\frac{1}{2}}$ axis, $dE_m^{\frac{1}{2}}/(E_m^{\frac{1}{2}}dT)$, if it exists at all, is less than 5.9×10^{-5} deg.$^{-1}$.

INTRODUCTION

RECENTLY Phipps and Seifert[1] measured the electron emission from clean tungsten as a function of the applied electrical field and found that the Schottky equation,

$$i=i_0 \exp\left[(e^{\frac{3}{2}}E^{\frac{1}{2}})/(kT)\right],$$

in which i_0 is the specific electron current at zero field and E is the electrical field, is valid only as a first approximation. By plotting $\Delta \log_{10} i$, which is the deviation from a reference line calculated by the method of least squares, against $E^{\frac{1}{2}}$ a periodic curve was obtained, whose period and amplitude increased with increasing field. That investigation was extended to fields of 2.6×10^5 volts cm^{-1}. Later work by the same authors[2] indicated that for clean tungsten the periodic behavior continued to fields as high as 9×10^5 volts cm^{-1}, and that the electron current from clean tantalum deviated in the same manner as tungsten, to the highest field investigated, namely, to 2.6×10^5 volts cm^{-1}. The purpose of the present investigation was to determine more accurately the values of $E^{\frac{1}{2}}$ at which the maximal and minimal values of the deviation occur and to make a more careful study of the phenomenon above fields of 2.6×10^5 volts cm^{-1}.

EXPERIMENTAL

The electrical circuit for measuring the electron current and for controlling the temperature of the filament was the same as described by Seifert and Phipps.[2] The Jones-Langmuir[3] temperature scale for tungsten was employed in the previous work.[2] In the present investigation a correction was made for the fact, observed by Seifert and

[1] T. E. Phipps and R. L. E. Seifert, Phys. Rev. **53**, 493 (1938).
[2] R. L. E. Seifert and T. E. Phipps, Phys. Rev., preceding paper.
[3] H. A. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 310 (1927).