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The Surface Ionization of Potassium on Tungsten

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The surface ionization of potassium on tungsten has been investigated by a method which employed a ray of potassium atoms. The use of an atomic ray eliminated photoelectric currents and permitted observations of the degree of ionization to be made up to temperatures as high as 2800°K. Between temperatures of 1350° and 2170°K the graph of the logarithm of the ion-atom ratio *versus* $1/T$ is linear, and when corrected to zero field yields a value of work function for tungsten of 4.51 ±0.01 v. The intercept on the $\log_{10} i_+/i_a$ axis has a value very near to zero instead of the value $\log_{10} 1/2$, expected from theory. This difference between the experimental and the theoretical intercept is interpreted as evidence for a temperature coefficient of the work function. If $\phi=\phi_0+\alpha T$ expresses the temperature dependence of ϕ, α is calculated to have the value 5.6×10^{-5} volt degree^{-1}. It is suggested that the departure from linearity at high temperatures may be accounted for by assuming a temperature dependence in that range of the form $\phi=\phi_0+\alpha T+\beta T^2$.

Introduction

The surface ionization of caesium atoms on tungsten and tungsten oxide surfaces partly covered by an adsorbed layer of caesium has been exhaustively investigated by Langmuir[1] and others.[2, 3, 4] Killian[5] has carried out similar investigations upon potassium. The method employed by all the above investigators involved surrounding the ionization unit with the saturated vapor of the alkali metal. Attempts by them to extend the measurements to high temperatures where the surface of the wire would be free of adsorbed alkali metal were not successful because of the onset of large photoelectric currents from collector to wire at about 1500°K.

Recently Morgulis,[6] studying the ionization of sodium on a clean tungsten surface, also used the above method (referred to hereafter as the bulb method). He found in the case of sodium that photoelectric currents did not become serious until a temperature of 1700°K was reached; and by using a magnetron to turn back the photoelectrons, he was able to obtain measurements as high as 2200°K. From the measurement of the positive ion current at different wire temperatures and from vapor pressure data for sodium, Morgulis calculated approximate values for the percentage ionization of sodium on the tungsten surface. His values were in agreement as to order of magnitude with those to be expected from theory.

The authors recently reported[7, 8] upon a preliminary investigation of the surface ionization of potassium on tungsten, in which an atomic ray of potassium was employed. The use of an atomic ray was found to eliminate the photoelectric current, which proved troublesome at high temperatures in the bulb method. The present article describes the continuation of this work under improved experimental conditions, and discusses the agreement of the results with theory.

Theory

The theory of surface ionization has been discussed by Langmuir,[1] Becker,[4, 9] Fowler,[10] and others. To facilitate the discussion of results, a brief résumé of the theory is given here. For the reaction

$$K(g)=K^+(g)+E^-(g) \tag{1}$$

the numbers per cm^3 of ions, atoms, and electrons at equilibrium are related by the expression

$$\frac{n_+n_e}{n_a}=\frac{\omega_+\omega_e}{\omega_a}\left[\frac{2\pi m_ekT}{h^2}\right]^{\frac{3}{2}}\exp\left[-\frac{I\epsilon}{kT}\right], \tag{2}$$

where ω_+, ω_a, ω_e are, respectively, the statistical weights of ions, atoms, and electrons; m_e is the

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[1] I. Langmuir, Proc. Roy. Soc. **A107**, 61 (1925).
[2] Ives, Phys. Rev. **21**, 385 (1923).
[3] Meyer, Ann. d. Physik (5) **4**, 357 (1930).
[4] Becker, Phys. Rev. **28**, 341 (1926).
[5] Killian, Phys. Rev. **27**, 578 (1926).
[6] Morgulis, Physik. Zeits. Sowjetunion **5**, 221 (1934).
[7] Copley and Phipps, Phys. Rev. **45**, 344 (1934).
[8] Copley and Phipps, Phys. Rev. **46**, 144 (1934).
[9] Becker, Trans. Am. Electrochem. Soc. **60**, 153 (1929).
[10] Fowler, *Statistical Mechanics* (Cambridge Press, 1929), p. 268.

mass of an electron and I is the ionization potential of potassium. If in Eq. (2) we express n_e by

$$n_e=\omega_e[2\pi m_e kT/h^2]^{\frac{3}{2}} \exp[-\phi\epsilon/kT], \qquad (3)$$

where ϕ is the work function at temperature T, and ϵ is the charge on an electron, we obtain

$$n_+/n_a=(\omega_+/\omega_a) \exp[-(I-\phi)\epsilon/kT]. \qquad (4)$$

Eq. (4) may be modified by replacing the number of ions per cm^3, n_+, and the number of atoms per cm^3, n_a, by the number of ions, i_+, and number of atoms, i_a, which cross per second in one direction through unit area of an imaginary plane in the equilibrium enclosure. This leads to the equation,

$$i_+/i_a=(\omega_+/\omega_a) \exp[-(I-\phi)\epsilon/kT]. \qquad (5)$$

If equilibrium is assumed to be reached by a surface reaction, and no elastic reflection of the particles takes place, then Eq. (5) also gives the ratio of ions to atoms evaporating from the surface. If the possibility of elastic reflection is assumed, then the ratio of ions to atoms evaporating from unit area in unit time will be given by

$$\frac{i_+}{i_a}=\frac{(1-r_+)}{(1-r_a)}\frac{\omega_+}{\omega_a}\exp\left[\frac{-(I-\phi)\epsilon}{kT}\right]. \qquad (6)$$

In the present work, a ray of atoms from a source not at the same temperature as the wire is used. If a reflection coefficient for atoms exists, it is possible that it might differ from the one in Eq. (6). However, Taylor and Langmuir[11] have shown that the reflection coefficient of caesium atoms, coming from a source at a low temperature and striking a clean tungsten wire, is zero at wire temperatures as high as 1500°. It seems very likely that the reflection coefficient of potassium atoms on tungsten is also zero. Taylor and Langmuir[11] also discuss the reflection coefficient of positive ions and conclude that, on account of the strong attractive forces between ions and a tungsten surface, it is very likely that r_+ is zero. If these assumptions are justified, then the ratio of ions to atoms coming from the wire should be

$$i_+/i_a=\tfrac{1}{2} \exp[-(I-\phi)\epsilon/kT], \qquad (7)$$

where ω_+ is replaced by 1 and ω_a by 2. The degree of ionization is given by

$$(i_+/i_a)/(i_+/i_a+1). \qquad (8)$$

The determination of i_a requires a knowledge of the total number of atoms striking the wire. This is determined by coating the wire with an activated layer of oxygen atoms, which raises the work function of tungsten to such a high value that complete ionization is obtained. The value of i_a is then given by

$$i_a=i_{\mathrm{WO}}-i_+, \qquad (9)$$

where i_{WO} is the total number of atoms striking the wire.

The value of i_+/i_a in Eq. (7) is its value at zero field. Most of the data in this work were obtained with a potential drop of 45 volts between filament and cage. Taylor and Langmuir[11] have shown for caesium on tungsten, and Morgulis[6] for sodium on tungsten, that the positive ion current depends upon the voltage. For this reason, the effect of the voltage on the positive ion current was studied. Morgulis[6] has discussed this voltage effect and has deduced the following relationship between the ion-atom ratio with a field E at the surface of the wire, and its value at zero field,

$$\log_{10}\left(\frac{i_+}{i_a}\right)_E=\log_{10}\left(\frac{i_+}{i_a}\right)_0+\frac{Ex_0\epsilon}{2.303k}\cdot\frac{1}{T}, \qquad (10)$$

x_0 is the distance from the surface at which ionization takes place. It is to be noted that the relation between $\log_{10}(i_+/i_a)_E$ and E should be linear, and that the slope of the line obtained should vary inversely with the temperature. Another way of regarding the voltage effect is to consider it as an exactly inverse Schottky effect. In this case there should be a linear relationship between $\log_{10}(i_+/i_a)_E$ and $E^{\frac{1}{2}}$. Both methods have been used in the treatment of the data. It will be shown that by either method the correction to zero field is so slight as to be almost negligible.

Apparatus and Materials

Fig. 1 shows the essential features of the apparatus. The furnace is below; the detector chamber is above. The inner part of the furnace has imbedded in its surface a glass-sheathed

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[11] Taylor and Langmuir, Phys. Rev. **44**, 423 (1933).

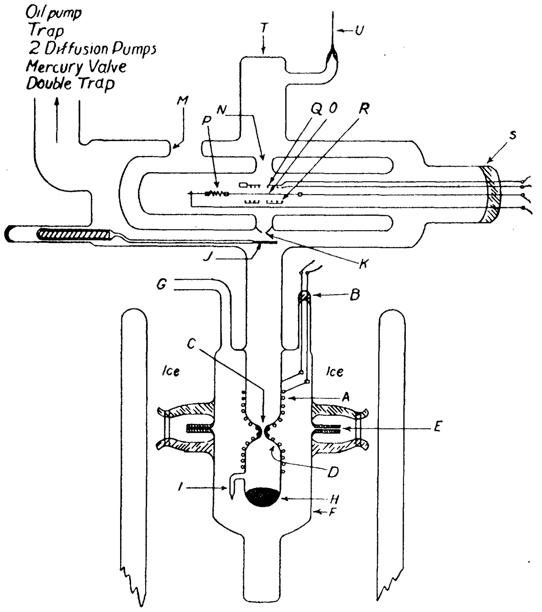

FIG. 1. Diagram of apparatus, detection unit (above) and furnace (below).

10-mil (0.025 cm) tungsten wire *A*, which serves as a heating element. This element is spot-welded to 40-mil (0.1 cm) tungsten wires which lead to the outside through the vacuum seal *B*. The furnace opening *C* is a capillary 0.07 cm in diameter. Below the furnace capillary *C* the inner wall *D* was heavily platinized by a preliminary evaporation process. Without this platinization the ray was observed to fluctuate seriously, due perhaps to the crawling of liquid potassium into the capillary. A ring-sealed vacuum jacket, separable at *E*, encloses the furnace. The inner walls of this jacket *F* are chemically silvered to reduce radiation losses, and a high vacuum is maintained about the furnace through the tube *G*. The outer walls of the jacket and the temporary beeswax-paraffin seal at *E* are kept at ice temperature. The pool of potassium *H* is introduced from a distillation train through *I* before the outer jacket is assembled. A constant current (about 1 ampere) from a storage battery of large capacity serves to maintain an extremely constant ray of potassium over long periods of time.

In the detection unit, above, *J* is a magnetically operated shutter, which serves to interrupt the atomic ray. *K* is a thin-walled circular orifice about 0.07 cm in diameter in the liquid-air cooled insert *M*, which serves to define the atomic ray. The opening *N* in the insert permits direct observation at all times of the wire *O* through the optical window *T*. This facilitates the alignment of the wire with the atomic ray. At the center of the detector unit is the tungsten wire *O*, 5 cm in length and 0.0051 cm in diameter, held taut by a tungsten spiral *P*. Specifications for this spring were taken from Langmuir and Blodgett.[12] Concentric with the wire is a nickel cylinder *Q*, 2 cm in length and 1 cm in diameter, provided with slots about 0.3 cm wide and 0.5 cm long on opposite sides from each other in the ray direction. For outgassing the cylinder and for removing the accumulated potassium from its inner surface during an experiment, a spiral grid *R* is provided. This consists of about 10 turns of tungsten wire 0.03 cm in diameter, which at one end is fastened rigidly to the plate, and at the other is spot-welded to a heavy tungsten lead-out.

U is a thick-walled, very fine capillary which permits the coating of the wire *O* with oxygen by occasional admission of air.

A "GM" galvanometer with a scale located 5 meters away from the galvanometer was used to measure the positive ion current. A phosphor-bronze suspension was used to eliminate zero drift. The sensitivity of the set-up was 1×10^{-10} ampere/mm.

The current for heating the tungsten filament *O* was supplied by storage cells and was regulated by a continuously varying resistance. The current was measured by a carefully calibrated Weston milliammeter. The temperature of the tungsten filament was calculated by the current-temperature-diameter function of Jones and Langmuir.[13] At low temperatures, lead loss corrections were calculated.[14]

The tungsten wire was of high purity and was furnished through the courtesy of Mr. B. Benbow, by the Incandescent Lamp Department of the General Electric Company, Nela Park, Cleveland. The potassium was obtained through the courtesy of Mr. H. N. Gilbert from the

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

[13] Jones and Langmuir, Gen. Elec. Rev. **30**, 310, 354 (1927).

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

Chemical Division of the R. and H. Chemicals Department of the du Pont Company, Niagara Falls, N. Y. It was stated that this metal had not come in contact with oil, and that its only impurity was about one percent of sodium. It was given a fractional distillation for further purification and sealed off in a glass capsule for later use.

Procedure

The apparatus shown in Fig. 1 was sealed to a vacuum line which consisted of the following parts in order: two liquid-air traps, two mercury diffusion pumps in series, a liquid-air trap, and a Hyvac oil pump.

With the lower half of the furnace jacket removed, a distillation train was attached at *I*. The distillation train held a capsule of potassium and a magnetic hammer for breaking the capsule in the vacuum. The entire apparatus was then surrounded by a furnace and heated to a temperature between 450° and 500°C for a period of several hours; meanwhile the vacuum line was heavily torched as far back as the nearest diffusion pump. Liquid air was put on the trap nearest the diffusion pump on the apparatus side. The grid *R* was then heated by passing a large current through it to outgas both *R* and *Q*. The wire was aged according to the directions of Taylor and Langmuir.[11] After aging the filament, liquid air was placed on the trap nearest the apparatus. The vacuum was tested by noting the constancy of electron emission after flashing the filament to a high temperature to remove any adsorbed gas. Under the best conditions, even without liquid air in the insert *M*, the electron current did not diminish over a period of several hours. Ordinarily, however, extremely constant emission was not obtained until *M* was cooled with liquid air.

When the vacuum appeared to be satisfactory, the capsule was broken and approximately 50 percent of the potassium was distilled into the furnace; the distillation train was then sealed off at *I*. The chemical silvering of the walls, mentioned above, was now carried out and the furnace space was evacuated.

M was then filled with liquid air, the shutter *J* opened, and the tungsten filament heated to approximately 1500°K. The storage battery current through *A* was adjusted until a constant galvanometer deflection of approximately 150 mm was obtained. This deflection corresponded to a rate of arrival at the wire of approximately 1×10^{11} atoms sec.^{-1}, or to a specific rate of 6×10^{13} atoms cm^{-2} sec.^{-1}.

Galvanometer deflections, i_+, were then noted for a series of wire temperatures. At the end of such a series, the wire was brought to a temperature at which a complete activated layer of oxygen would form upon it (1640°K was used throughout this work), and air was admitted cautiously until a maximum galvanometer deflection was obtained. This value, i_{WO}, was taken as equal to the full beam at all of the temperatures of the series. As a check, the wire was then flashed to remove the oxygen layer, and the deflection at 1640° on the clean surface was again observed. The ratio (i_+/i_{WO}) at 1640°K was found to be the same by the two methods. This procedure was repeated at will until the degree of ionization at 1640° was well established. It was found advisable, however, to leave this step until the end of a series of experiments as the vacuum deteriorated somewhat after admission of air. Values of i_a at each temperature were then calculated by Eq. (9), and a value of $\log_{10}(i_+/i_a)$ was determined for each temperature.

The procedure given in the above paragraph is a somewhat idealized one, which was practicable in case the beam remained constant over long periods of time. Actually, in most experiments, small drifts in the beam were observed over the time interval necessary for the taking of a series of i_+ values and the determining of i_{WO} for the series. These drifts in the beam intensity made the following procedure necessary. 1640°K was used as a standard temperature with respect to which fluctuations in the beam intensity could be computed. Deflections were observed at 1640°K both before and after observation at each of the other temperatures; the mean of the two bracketing values at 1640°K was taken as the correct value of i_+ at the time when the bracketed value was taken. In this way the effect of slow drifts in the intensity of the ray was annulled.

At temperatures above 2400°K photoelectric currents were frequently observed. Thus, with the wire at 2400°K, a deflection of a few millimeters might be observed after the shutter was closed. To minimize this effect, it was found desirable to keep the shutter closed, except during the actual reading of the galvanometer, and to heat out the collector cylinder Q (by heating the grid R) at frequent intervals; this treatment invariably reduced the residual photoelectric current to a very small value, which could be corrected for without introducing a serious uncertainty into the i_+ values.

In observing the effect of voltage upon the ionization, the following procedure was adopted. The i_+ value at a standard voltage (45 volts) and at the standard temperature (1640°K) was employed as the bracketing value. The bracketed value was the deflection at any nonstandard temperature and nonstandard voltage. Since i_{WO} may reasonably be assumed to be independent of voltage, a single determination of it is sufficient for the calculation of i_a values at all voltages and temperatures.

Results

Fig. 2 shows a plot of the data[15] obtained in two different apparatuses, plotted to the axes $\log_{10}(i_+/i_a)$ *versus* $1/T$. Throughout these experiments the collector cylinder Q was negative approximately 45 volts with respect to the negative end of the filament, which corresponded to a field at the surface of the wire of about 3350 volts cm^{-1}. (The correction to zero field is presented later.)

The value of $\log_{10}(i_+/i_a)$ at standard temperature is shown by the solid black circle. This point was calculated by using the mean of seven independent determinations of the degree of ionization, i_+/i_{WO}; namely, 0.800, 0.800, 0.796, 0.790, 0.796, 0.806, and 0.800. The mean of these, 0.7983, was used in calculating the values of $\log_{10}(i_+/i_a)$ at all other temperatures. An example will serve to show the method: i_+ at $T=1887$°K ($1/T\times10^5=53$) was 134.4 (in arbitrary units). For the same beam, the mean of the bracketing values at $T=1640°$ was 139.75. Whence, $i_{\mathrm{WO}}=139.75\div0.7983=175.06$; $i_a=175.06-134.4=40.66$; $i_+/i_a=134.4\div40.66=3.3054$; $\log_{10}(i_+/i_a)=0.5192$. This is one of the six points plotted at $1/T=53$.

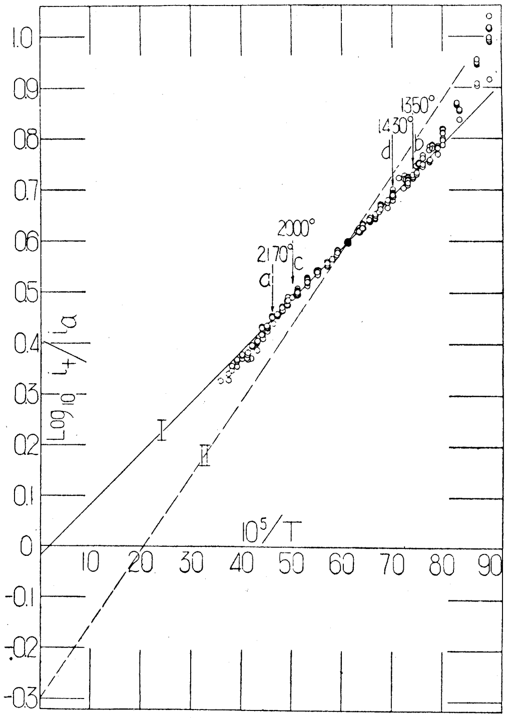

FIG. 2. Plot showing the linear region ab represented by line I, and the deviation from linearity above 2170°K and below 1350°K. The solid black circle represents the temperature at which the degree of ionization was determined.

It will be observed that between a and b the points lie on a straight line. The solid line I is the best line through the 105 points which lie between a and b,—as determined by a least-squares method. The equation of this line is

$$\log_{10}(i_+/i_a)_{E\leqq3350}=1007.3/T-0.0173. \quad (11)$$

To the left of a (temperatures above 2170°K), the experimental points lie below I; to the right of b (temperatures below 1350°K) the points lie above I, and the deviation from the mean of the points in a cluster at the same $1/T$ value becomes much greater than in the range ab.

The limits a and b of the linear region were set somewhat arbitrarily. To show the effect upon slope and intercept of choosing narrower limits, the equation of the best straight line through the 71 points which lie between c and d was also determined by the method of least squares. This line (not shown in Fig. 2) had for its equation

$$\log_{10}(i_+/i_a)_{E\leqq3350}=(989.25\pm8.20)/T-0.0055\pm0.005. \quad (12)$$

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[15] Tables of data are omitted at the suggestion of the editor.

It thus appears that the intercept of the best line through the narrower region *cd* deviates from zero by an amount which is approximately equal to its probable error. The possibility must therefore be considered that the true value of the intercept is zero, and that the deviation observed is without significance. This point will be discussed later.

Completely satisfactory explanations for the deviations at high and at low temperatures have not as yet been found. That they are not explainable by a defect of apparatus (such, for example, as a lateral shifting of the wire into or out of the beam due to a dissymmetry in the action of the spring) is indicated by the fact that in two preliminary, as well as in the two final apparatuses, deviations were observed at approximately the same $1/T$ values, and always in the same direction. As a direct check upon wire movement, a traveling microscope was focused upon the wire through the optical window, and the wire was observed while its temperature was varied from room temperature to 2800°K. No lateral motion could be detected. However, since a very small motion would be sufficient to explain the deviations observed we do not think that this possibility is entirely excluded in the high temperature region. In future work, it is proposed to remove this uncertainty by replacing the circular orifice at K with a slit which has accurately parallel sides.

The low temperature deviation is thought not to be due to the above cause. It may, however, have been caused by adsorption on the wire of some gas, other than oxygen, which was present in the apparatus. The greater deviations from the mean in that region are accounted for by the fact that i_a becomes small compared with i_+, and that small errors in the determination of i_a are magnified in the quotient.

With regard to the deviation at high temperatures (in the region to the left of a, Fig. 1) there appeared to be some evidence of an effect of apparatus upon the course of the curve. Points taken with the second apparatus lay somewhat closer to the line than those taken with the first apparatus. (These points have not, however, been distinguished in the plot.) That the deviations are not due to a photoelectric effect is apparent, since this would tend to give values of $\log i_+/i_a$ above the line. An explanation which suggests itself is that a term in the temperature coefficient of the work function involving a power of T higher than the first becomes significant at temperatures above 2170°K. The same phenomenon has been observed in unpublished measurements which have been made in this laboratory upon the surface ionization of caesium on tungsten.

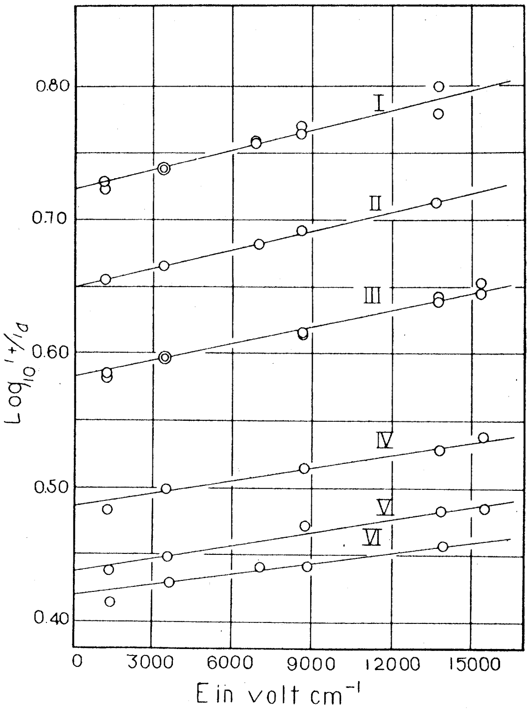

FIG. 3. The effect of field at different temperatures upon ion-atom ratio. I, $T=1337$°K; II, $T=1479$°K; III, $T=1640$°K; IV, $T=1961$°K; V, $T=2174$°K; VI, $T=2381$°K. Values of the ratio,

$$\log_{10}(i_+/i_a)_{E=0}/\log_{10}(i_+/i_a)_{E\simeq 3350},$$

for the six temperatures given above are, in order: 0.975, 0.975, 0.977, 0.978, 0.975, 0.977.

The difference between the first two resonance levels of potassium and the ground level is small enough so that at the highest temperature in the linear region ab (I, Fig. 2) no appreciable change in the ion-atom ratio would result from a correction of the heat capacity and entropy of potassium for internal excitation. However, between 2200° and 2800°K the contribution of internal excitation is no longer negligible, and is in a direction to make the curve to the left of a bend upward. Actually the curve bends downward.

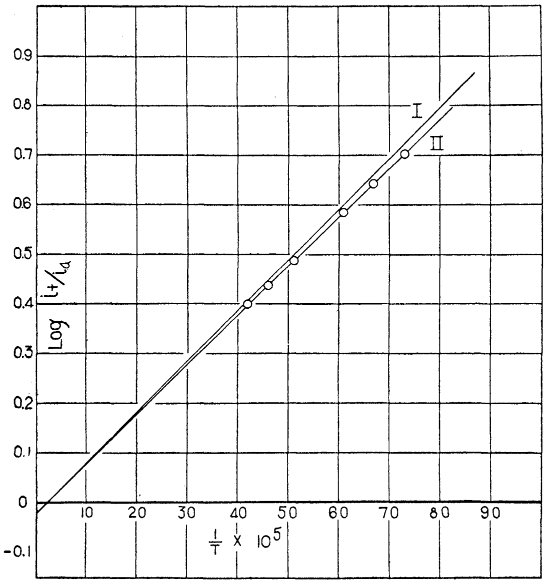

FIG. 4. The correction to zero field (line II) of the data plotted in Fig. 2 (line I).

Since the data in this region were not satisfactorily reproducible, no correction for internal excitation has been made.

Fig. 3 shows a plot of $\log_{10}(i_+/i_a)$ *versus* E, the field at the surface of the wire, for values of the field between zero and 15,000 volts cm^{-1}. It is seen that the relation is linear between 3000 and 15,000 volts cm^{-1}, and that the slopes decrease in the series I to VI as the temperatures increase. The products of T times slope in this series are, respectively: 0.48, 0.51, 0.49, 0.46, 0.53, and 0.50 volt^{-1} cm degree. This constancy of T times slope is in agreement with Eq. (10); however, it is in disagreement with the results of Morgulis,[6] who observed no such constancy for sodium on tungsten.

The circled points in Fig. 4 are calculated in the following manner. Points calculated from Eq. (11) are corrected for voltage by multiplying them by the ratio,

$$\log_{10}(i_+/i_a)_{E=0}/\log_{10}(i_+/i_a)_{E\leqq 3350},$$

obtained from Fig. 3. Line I in Fig. 4 is identical with line I of Fig. 2; that is, it is the best line through the 45-volt values in the ab region. The equation of II (Fig. 4) is

$$\log_{10}(i_+/i_a)_{E=0} = (987.24 \pm 8.20)/T - 0.0188 \pm 0.005. \quad (13)$$

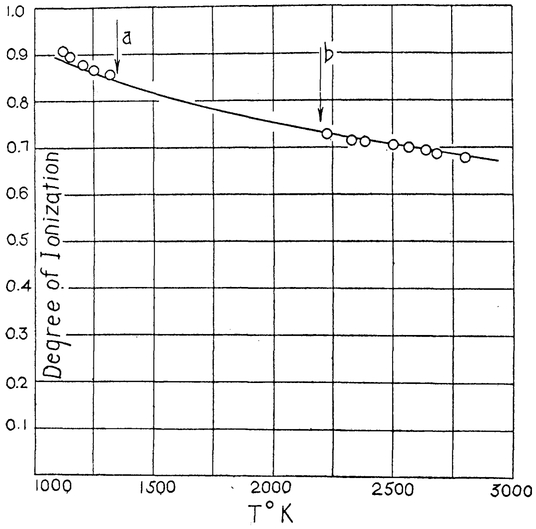

FIG. 5. The degree of ionization of potassium on tungsten at E of 3350 volt cm^{-1}. The heavy line is calculated from Eq. (11).

It is evident that the intercept is not appreciably changed by correcting to zero field. The slope is slightly diminished.

If the assumption (to be discussed later) is made that in the ab region of Fig. 2 the tungsten surface is clean—that is, free of adsorbed potassium or of electronegative gas—then from (13) and (7) we may write

$$(\phi - I)\epsilon/k = 987.24 \times 2.3026, \quad (14)$$

and have upon substituting numerical values

$$\phi - I = 0.196 \pm 0.002 \text{ v.} \quad (15)$$

Since I for potassium is 4.318 v, we obtain for ϕ a value of 4.514 ± 0.002 v. The probable error ± 0.002 depends upon the assumption of correctness of temperature in the least squares calculation. If Langmuir's current-diameter-temperature function for tungsten is assumed correct, we estimate that the maximum uncertainty in temperature is $\pm 20°$, which corresponds to an uncertainty of ± 0.005 v in ϕ. Owing to experimental causes, then, the uncertainty in ϕ is of the order ± 0.01 v.

The data plotted in Fig. 3 were also plotted against $E^{\frac{1}{2}}$. There was more deviation from linearity in these plots. The product of T times slope of the best straight lines through the points at the various temperatures showed a greater trend than the values obtained by the first method. When the intercepts, $\log_{10}(i_+/i_a)_{E^{\frac{1}{2}}=0}$ were plotted against $1/T$, and a work function was calculated from the slope, a value of 4.504 v was obtained. There was no appreciable difference between the intercept obtained by this method and that obtained by the first method.

Fig. 5 shows the degree of ionization of potassium from tungsten as a function of the temperature. The heavy line was constructed by calculating the degrees of ionization from Eq. (11). To the left of a and to the right of b the circled points were calculated from mean values of the experimental clusters at various $1/T$ values in Fig. 1. It is seen, as in Fig. 2, that the experimental points lie high at low temperatures and low in the high temperature range.

Discussion of Results

In the calculation of ϕ by (14) and (15), only the region ab (Fig. 2) was considered; the assumptions were made (1) that the surface is clean at temperatures above 1350°K, and (2) that departures from linearity at high and at low temperatures arise from causes which are not operative or are unimportant in the region ab. It has been suggested to us that in this region a slight amount of potassium is adsorbed on the surface, sufficient to lower the work function by a few hundredths of a volt between the limits 2170 and 1350°K. Such an effect would lead to a curve concave toward the $1/T$ axis in this region. To explain the observed linearity one would have to assume a compensating effect such as the adsorption of an electronegative gas, which would raise the work function.

We have estimated the amount of potassium on a tungsten surface at 1350°K for the rate of arrival used in these experiments. The basis for this calculation was the data of Taylor and Langmuir[11] upon caesium. In making the calculation for potassium we have increased their value for the heat of vaporization of ions by fifteen percent. This estimation led to the conclusion that at 1350°K there was not sufficient potassium adsorbed on the tungsten in our experiment to lower the work function by as much as 0.01 volt. That this estimate is reliable is confirmed by the fact that we observed the positive ion current to decrease rapidly in the neighborhood of 1100°K, in agreement with the temperature at which adsorption becomes important as calculated by the method used above. In view of the above calculation we shall proceed with the discussion under the assumption that the surface was clean above 1350°K.

From the fact that a linear region is found in the plot of Fig. 2, we may conclude that the work function is either temperature independent, or that it has a temperature dependence in the linear region expressible by the relation $\phi=\phi_0+\alpha T$.

Let us consider first the case in which we assume temperature dependence. If we substitute the above value of ϕ into (6), and if we plot $\log_{10}(i_+/i_a)$ *versus* $1/T$, we see that the intercept on the $\log_{10}(i_+/i_a)$ axis is

$$\log_{10}(i_+/i_a)_{1/T=0}=\log_{10}\omega_+/\omega_a+\alpha\epsilon/2.3026k.$$

Substituting numerical values, we obtain for α a value of 5.6×10^{-5} volt degree^{-1}. The value for ϕ calculated from the slope of line II (Fig. 4) is its value at 0°K.

The Richardson line for tungsten is known to be straight in the same region of temperature as that in which the measurements under discussion were taken. Consequently the value of ϕ_0 obtained in this way should agree with the slope of the Richardson line for tungsten. Our value of 4.514 v agrees within experimental error with the value 4.52 v found by Dushman[16] for tungsten. In a recent article, Becker[17] has pointed out that α cannot be evaluated accurately from the intercept of the Richardson line. This comes about because i_e in the theoretical equation for the emission of electrons is the emission per cm^2 of effective surface. The apparent surface of a wire has been estimated to be 25 to 50 percent less than the effective surface. Consequently values of α calculated from the intercept of the Richardson line for tungsten will be too small. It should be noted that this difficulty does not arise in the calculation of α from our experimental results since surface does not appear in the theoretical relationship for the ion-atom ratio.

Dushman[16] obtained a value of 60 amp. cm^{-2} °K^2 for A from his measurements on the emission

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[16] Dushman, Rowe, Ewald and Kidner, Phys. Rev. **44**, 345 (1925).

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

of tungsten. If we apply a surface correction, this value will be reduced to between 30 and 45. Such a value for A gives a larger value for α than we obtained. In fact to bring the α of thermionic emission measurements into agreement with our value of α, an A sufficiently large to give a value —when corrected for surface—of 60 should have been observed. If we assume our measurements to be correct, then either (a) the experimental value of A obtained by Dushman is too low; or (b) the difference between effective and apparent surface is smaller than hitherto assumed. Measurements[18] made recently in this laboratory of the electron emission of tungsten filaments taken from the same spool as those used in this investigation gave a value of 96 for A, which would indicate a surface correction of more than 50 percent. A value for ϕ_0 of 4.62 v was obtained from these electron emission measurements. This value is 0.1 v higher than that obtained from the slope of line II (Fig. 4). We are at present unable to account for this discrepancy.

Let us consider next the case in which ϕ is assumed to be independent of the temperature. Here the intercept on the $\log_{10}(i_+/i_a)$ axis expected from theory is log (1/2)—that is, -0.301 —instead of the very small value -0.0188 which we obtained. This may be seen graphically in Fig. 2. Line II is the line expected from theory if ϕ is temperature independent. (The solid black circle is the "standard point" through which any experimental line must pass.) It is apparent that the assumption of a temperature independent work function will explain the data only if the ratio $(1-r_+)/(1-r_a)$ nearly cancels the ratio of the statistical weights in (6). As was pointed out in an earlier section, it does not seem likely that the ratio $(1-r_+)/(1-r_a)$ can differ by a sufficient amount from unity to do this.

Future experimental work will be directed toward improving the accuracy of the data in the high temperature range, and toward investigating other metal pairs which have $(\phi-I)$ values of the order of 0.2 to 0.3 v, and which are accordingly suitable for an investigation of this kind. From studies of this sort it should be possible to decide whether the near approach of the intercept on the $\log_{10}(i_+/i_a)$ axis to zero is fortuitous, owing to the existence of a temperature coefficient of tungsten of the order of magnitude required to raise the intercept to nearly zero, or whether (6) requires modification with respect to the omission of the ratio of the statistical weights.[19]

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[18] To be published.

[19] Anselm, Compt. rend. acad. sci. U. S. S. R. **3**, 332 (1934).