Positive and Negative Thermionic Emission from Columbium

H. B. WAHLIN AND L. O. SORDAHL, *Department of Physics, University of Wisconsin*

(Received April 4, 1934)

The positive ion and electron work functions have been determined for well outgassed columbium and found to be for the electrons 3.96 volts with A equal to 57 amp./cm²/degree² and for positive ions 5.52 volts. It has been found that by bombarding the ionization gauge at a high temperature the specimen could be contaminated so as to change the electron work function by about 16 percent. The effect of impurities on the positive ion work function has been studied and it is shown that these will in general cause an increase in this quantity.

IN a series of letters to the editor it has been shown by one of us[1] that certain metals when heated to a sufficiently high temperature will emit positive ions of the metals themselves. It has been known for a long time that all metals when first heated to incandescence will emit positive alkaline ions but as far as the writers have been able to tell the metallic ions have hitherto escaped detection.

These findings have been verified by Smith,[2] who independently noted the emission of ions, which he concluded had a greater mass than the potassium ions, from tungsten. Later[3] he made a qualitative determination of the positive ion work functions for tungsten and molybdenum after determining the mass of the ions. Barnes[4] has extended and verified the results listed above and in addition has repeated Smith's determination of the work function for molybdenum. He obtained a value of 8.12 volts. This is about two volts higher than that obtained by Smith. Both these values are questionable due to insufficient heat treatment of the specimens used.

In the work described below the work functions for the electrons as well as for the positive ions has been determined for columbium, precautions being taken to eliminate spurious effects as much as possible.

EXPERIMENTAL PROCEDURE

An accurate determination of the work function, thermionically, requires that the temperature of the metal under investigation shall be known with considerable accuracy. This is particularly true if a reliable value of the constant A in the thermionic equation is desired.

Since the value of the emissivity used in computing the true temperature from the brightness temperature as determined with an optical pyrometer, may be a function of the outgassing, it was necessary to determine this quantity under good vacuum conditions. Mr. L. V. Whitney made such a determination using the wedge method. The optical pyrometers used followed the design proposed by Fairchild and Hoover.[5] The brightness and true temperatures are listed in Table I.

TABLE I. *Brightness temperature, T_B, and true temperature T_T, for $\lambda = 6690°A$.*

T_B°K	T_T°K	T_B°K	T_T°K
1200	1266	1650	1784
1250	1325	1700	1841
1300	1383	1750	1898
1350	1440	1800	1957
1400	1497	1850	2016
1450	1555	1900	2077
1500	1611	1950	2139
1550	1670	2000	2203
1600	1726		

The first thermionic determinations were made with a two guard ring tube (Fig. 1). G_1G_2 are the guard rings and C the collecting cylinder. Q_1Q_2 are two quartz rods which clamped the collector and guard rings in place. The collector was 25

[1] H. B. Wahlin, Phys. Rev. **34**, 164 (1929); **35**, 653 (1930); **37**, 467 (1931); **38**, 1074 (1931); Nature **123**, 912 (1929).

[2] L. P. Smith, Phys. Rev. **33**, 279 (1929).

[3] L. P. Smith, Phys. Rev. **35**, 381 (1930).

[4] L. L. Barnes, Phys. Rev. **42**, 487, 492 (1932).

[5] Fairchild and Hoover, J. O. S. A. and R. S. I. **7**, 542 (1923).

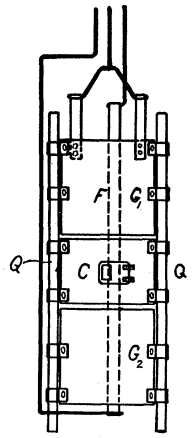

FIG. 1. Diagram of two guard ring tube.

mm in diameter and 25 mm long. The guard rings were about 40 mm long. The filament F, a strip of columbium 15 cm long, 2 mm wide, and 0.05 mm thick was held along the axis of the system of cylinders. The metallic parts of the tube were first heated in a vacuum to a final temperature of about 1300°C by electron bombardment. This heating extended over a period of 200 hours. The cylinders were then transferred to the main experimental tube and this sealed to the vacuum system as soon as possible. In all, the cylinders were exposed to the air for about 24 hours. Care was taken in handling the cylinders after outgassing to avoid contamination which may cause appreciable alkaline ion currents when the metal becomes warm.

The tube was evacuated and baked at a temperature ranging from 300°C to 400°C for a period of 250 hours. During the latter part of this baking the filament was heated to a final temperature of 1700°K. The furnace was then removed and the heating of the filament continued at a temperature of 1900°K for a total period of 1400 hours.

Fig. 2, curve A, shows a plot of $\log_e i - 2\log_e T$ against $1/T$ for electron data obtained after about 700 hours outgassing. As will be noticed, this curve shows a distinct break. The values of the work functions for the two parts of the curve are: for the high temperatures 4.0 volts and for the low temperatures 3.3 volts. With continued outgassing the break diminished until in the final stages it disappeared entirely (curve B). The final value obtained for the electron work function was 3.95 volts. The constant A was found to be 57 amp./cm^2/degree^2, a good check with the theoretical value of 60.2. The value of φ and A given above did not vary during the last 200 hours of heat treatment.

In the tube used in the above determinations the insulation between the cylinders was not sufficiently good to allow accurate measurement of the very small positive ion currents. Therefore the single guard ring tube (Fig. 3) with a loop filament was substituted. In this tube the collector (C) was supported from below and the filament (F) and guard ring (G) was held from a seal at the top. A disk shielded the lower seal from metallic vapor and thus prevented leakage across the glass. The tube was made sufficiently long so that the lower seal could be maintained at room temperature with the filament hot. The ionization gauge used in measuring the pressure was sealed to the evacuating lead about 25 cm from the experimental tube. The baking and outgassing process was approximately the same as for the first tube and extended over a total period of 1600 hours.

The first determinations of the electron work function made after 400 hours outgassing gave a value of 3.5 volts. The break which had appeared with the first specimen was entirely absent. With further outgassing this value rose until after 900 hours it had reached a value of 3.96 volts. The pressure at this time was about 7 $\times 10^{-8}$ mm.

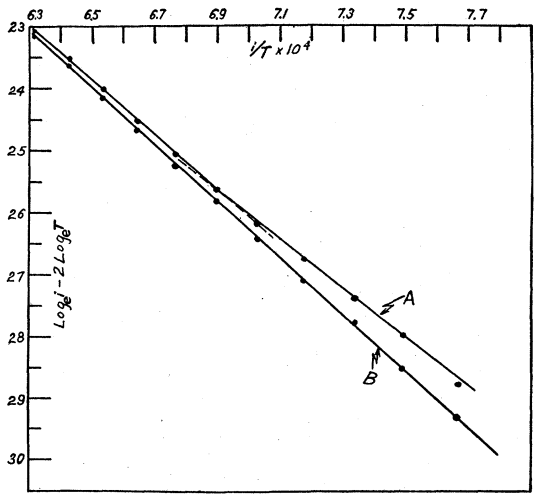

FIG. 2. Plot of $\log_e i - 2\log_e T$ against $1/T$.

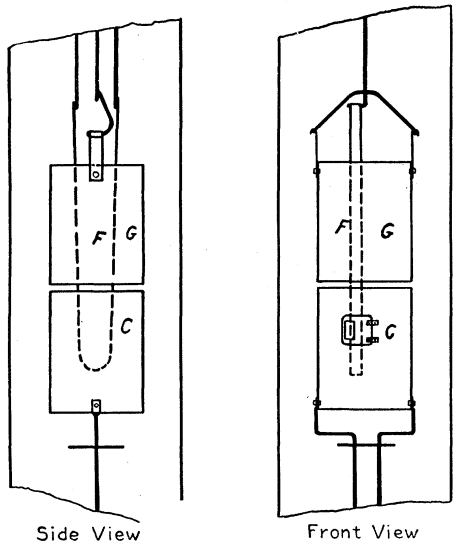

FIG. 3. Diagram of single guard ring tube.

The ionization gauge was then outgassed by bombardment at a temperature higher than that ordinarily used. After this bombardment the break appeared in the Richardson plot. The two values found for φ were 3.9 and 3.4 volts. Further heat treatment of the filament for 100 hours caused the break to disappear and the work function returned to a value of 3.96 volts. This value persisted over a total outgassing time of 1400 hours. In the meanwhile the pressure had dropped to less than 4×10^{-8} mm. A further change in the pressure to a final value of 10^{-8} did not change the results.

POSITIVE ION WORK FUNCTION

After 1400 hours outgassing, determinations of the positive ion work function were made. For this a quadrant electrometer with a current sensitivity of 4×10^{-12} amp./mm was substituted for the galvanometer used in measuring the electron space current. In order to shield the experimental tube from electrostatic effects the glass was given a coating of aquadag which was grounded. This was so satisfactory that air could be blown against the tube to cool it without the electrometer being disturbed.

The initial work function determination between the temperature limits of 2000°K and 2200°K was about 7.9 volts. Between 1800°K and 1950°K, with a higher electrometer sensitivity, a value of 5.4 volts was obtained. A continued flashing of the filament at the higher temperatures caused a lowering of the space current and also a lowering of the high temperature work function until a final value of 5.52 volts was obtained for both temperature ranges.

These values were computed from the equation

$$i=BT\ \text{exp.}\ (-\varphi/kT).$$

The value of B in this equation was found to be approximately 0.1 amp./cm²/degree. The above equation is admittedly approximate. Smith[2] has derived a more exact equation which unfortunately cannot be applied in this case due to a lack of the necessary information about columbium. However, a more exact equation should not change the value of φ greatly.

Fig. 4 shows a plot of $\log_e i-\log_e T$ against $1/T$ for the positive ion currents.

During the last 100 hours of flashing treatment the positive ion currents and the work function remained constant within the limits of error, and they remained the same whether the readings were taken by changing the temperature continuously or by reducing it between readings to some lower temperature (1200°K) to keep the walls of the tube cool.

After the observations on the positive ion currents had been concluded, the electron work function was again determined and was found to be 3.97 volts. The pressure as indicated by the

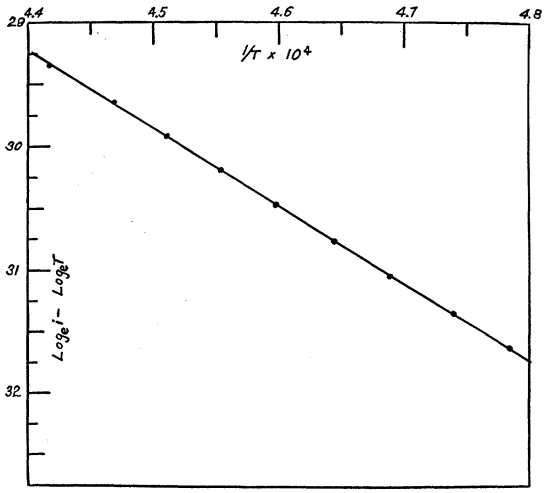

FIG. 4. Plot of $\log_e i-\log_e T$ against $1/T$ for positive ion currents.

ionization gauge was 10^{-8} mm. The average value for the electron work function from the specimens is thus 3.96 volts after correction for the Schottky effect.

The ionization gauge was now bombarded at a high temperature and again the break in the electron work function curve appeared. Heat treatment of the filament caused it to disappear as before.

Discussion of Results

The fact that the break in the electron work function curve did not appear with the second tube until after bombardment of the ionization gauge at a higher temperature than is generally used before pressure readings are taken shows conclusively that it is not characteristic of the filament. The fact that it disappears gradually and also is independent of the pressure indicates that some condensable material is volatilized from the gauge and condenses in the experimental tube. This is borne out by the fact that the break was more prominent if the bombardment was carried out with the experimental filament cold.

The vapor pressure of such a material would be determined by the temperature of the experimental tube which in turn is determined by the temperature of the filament. If the amount of the filament covered by this impurity is determined by the vapor pressure, one would expect that with continued heat treatment and as the material diffuses to the colder parts of the tube, the amount of the filament covered would be less and consequently the low temperature work function would approach the value characteristic of the pure metal.

The change in the positive ion work function is more satisfactorily explained. It is impossible to heat treat the filament for long periods at or above the temperatures at which it emits metallic positive ions since these ions generally become measurable only at temperatures where the vapor pressure becomes appreciable. If impurities which condense on the colder parts of the tube are given off during the early stages of outgassing, an equilibrium condition will be reached, with prolonged outgassing, where the vapor pressure due to these impurities will be negligible. If now the filament temperature is increased, the equilibrium will be disturbed due to the increased temperature of the colder parts of the tube and some of the impurity will volatilize. Some will also come from the comparatively cold ends of the filament. Such impurities (particularly if they are alkaline in nature) may become positively ionized on striking the hot filament and would increase the positive ion current. As the temperature of the filament is increased, this "impurity current" would increase rapidly and would tend to increase the work function. Continued flashing at the higher temperatures would establish a new equilibrium, and the effect of the impurities should disappear. Such an effect due to impurities may account for the discrepancy between Smith's and Barnes' results on molybdenum.