The Thermionic Constants for Platinum

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(Received July 24, 1933)

The thermionic constants for platinum in the form of cylindrical filaments were investigated. The slope of the supersaturation curves was taken as a criterion of filament condition. It was found that a very stable state, probably not indicative of a pure surface was obtained which withstood aging at 1650°K for 175 hours. For this condition the ϕ and A values are very high. Aging at 1785°K produced a new surface for which the supersaturation slopes were correct, and for which the constants were assumed to be approaching correct values. If A is taken to be 60 amp./cm²·deg.², ϕ is estimated to be 5.29 volts.

INTRODUCTION

THERMIONIC emission of platinum has been the subject of numerous investigations.[1] The most recent and significant has been that of DuBridge[2] who was able to check the thermionic with the photoelectric work function. His best values are: $\phi=6.27$ volts and $A=1.7\times10^4$ amp./cm²·deg.². The present paper deals with an attempt to evaluate these constants by an independent method.

Some earlier work[3] with tungsten has shown the adaptability of Schottky curves for indicating filament conditions. For constant temperatures ln I plotted against $(dv/dx)^{\frac{1}{2}}$ should, in the supersaturation region, give straight lines having a slope of $e^{\frac{3}{2}}/kT$. Unless the filament was in excellent condition these curves were very erratic; but a value of e correct to 0.2 percent was obtained under conditions where the curves were smooth straight lines. Similar experiments applied to platinum are described below. This method does not lend itself to photoelectric measurements, but possesses the advantage that cylindrical filaments may be used instead of strips. These withstand aging at much higher temperatures because of their smaller area and the reduced effect of local heating.

TUBES

The filaments used were wires of 5, 7 or 10 mil diameter and were of the purest platinum obtainable from Baker and Company, Newark, N. J. The manufacturers state that there are generally present spectroscopic traces of iron, magnesium and calcium. Anodes and guard rings were of 5 mil nickel. The tubes were of two types as shown in Fig. 1. Both are satisfactory but the type at the left is subject to the disadvantage that the tungsten spring may become permanently extended during bakeout, thus allowing the filament to become eccentric. However, the resultant change in gradient may be calculated, and is quite small.

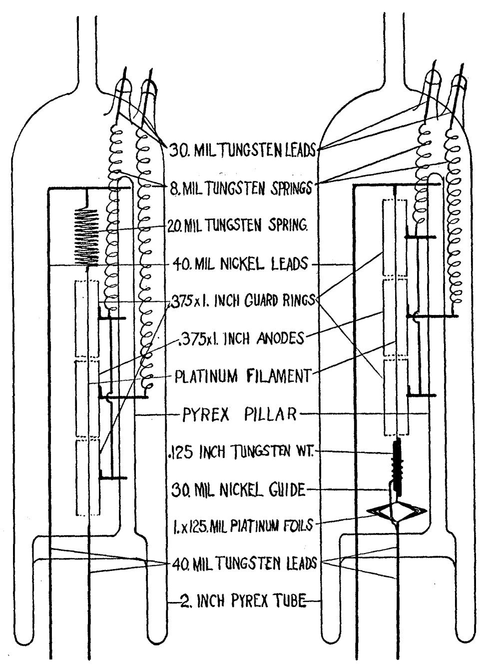

FIG. 1. Diagram of tube.

[1] Dushman, Rev. Mod. Phys. **2**, 396 (1930).
[2] DuBridge, Phys. Rev. **31**, 736 (1928); **32**, 961 (1928).
[3] Van Velzer and Ham, Phys. Rev. **33**, 1081 (1929).

Charcoal was used with liquid air on all tubes during operation and in some, magnesium was flashed into an auxiliary bulb immediately before beginning runs. The presence of charcoal bulbs necessitated a long bakeout. This was continued at temperatures of from 450 to 490°C for from 200 to 600 hours, after which the pressure with ovens on was between 10^{-4} and 10^{-5} mm of Hg. Liquid air was introduced around a trap on the system before the end of the bakeout. After baking, the metal parts were heated by a high frequency current and the filament was flashed at about 1750°C, in some cases for several hours. The pressure was now about 10^{-7} mm of Hg. Immediately after seal-off all of the joints were coated with Canada Balsam as a precautionary measure.

No attempt was made to measure the pressure in the tubes after removal from the pumps; but tungsten filament tubes of similar design and exhaust have been so tested by connecting their elements in an ionization gauge circuit with anode as plate and guard rings as collectors, the usual voltages being employed. This arrangement has been found to be about six times as sensitive as the usual design, but after liquid air had been placed around the charcoal for several hours (required for temperature equilibrium) the positive ion currents were less than 10^{-9} ampere.

The circuit diagram is shown in Fig. 2. The anode circuit includes, in series, a calibrated resistor of from 10^6 to 10^9 ohms. The potential across this was determined with a Compton electrometer set at a stable value of about 340 mm/volt.

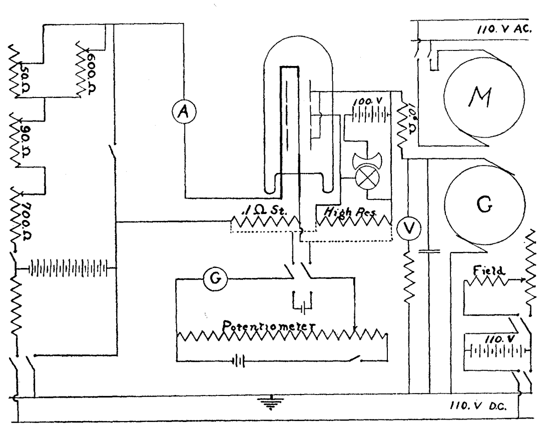

Fig. 2. Circuit diagram.

Temperature Scale

The determinations made were based on the temperature current relations given for tungsten by Langmuir and Jones.[4] Emissivities were corrected from the data of Forsythe.[5] In all cases crossed or nearby platinum and tungsten filaments were equated in brightness by viewing them through a telescope. Comparisons were made over a range of from roughly 1000°K to 2000°K. The final relation between heating current and absolute temperature is a weighted least square solution obtained from 170 points. In terms of a filament one centimeter in diameter it is expressed as $T=0.44460I+43.220I^{\frac{1}{2}}+315.40$. The probable error in the region investigated is 1.2°C.

Procedure

The charcoal was immersed in liquid air for several hours to attain temperature equilibrium. The filament was then heated to some aging value, usually of from 1650 to 1790°K; and runs were taken each 24 hours. At the beginning of each run the electrometer sensitivity was determined and tests made for electrical leakage. With the filament current held constant by means of the potentiometer, thermionic currents were then measured at anode potentials from 150 to 1250 volts.

Results

As aging progressed, four distinct types of characteristics were noted. At first the currents were large and erratic, usually increasing with time unless the filament temperature was raised above a critical value. The Schottky curve obtained with such filaments is shown in Fig. 3.

Second, there was a rather protracted stage, lasting in one case for 175 hours at an aging temperature between 1650 and 1690°K. This condition is characterized by Schottky slopes of from two to five times the theoretical value, which slopes sometimes increased at first, then decreased. The curves, too were not straight but concave downwards, though in the later runs they tended to straighten. As aging proceeded the consistency of the data increased and the

[4] Jones and Langmuir, G. E. Rev. 310 (1927).

[5] Forsythe, Int. Crit. Tables, Vol. V, 245.

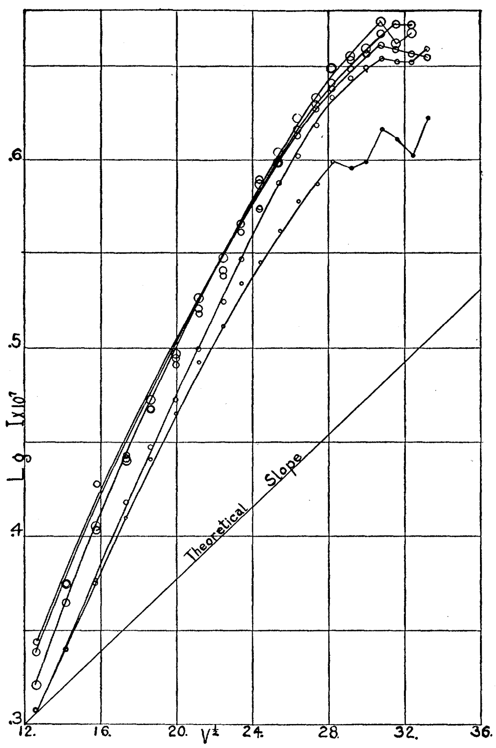

FIG. 3. Schottky curves during first stage for 7 mil filament. Aging has been preliminary, curves are erratic, slopes are high.

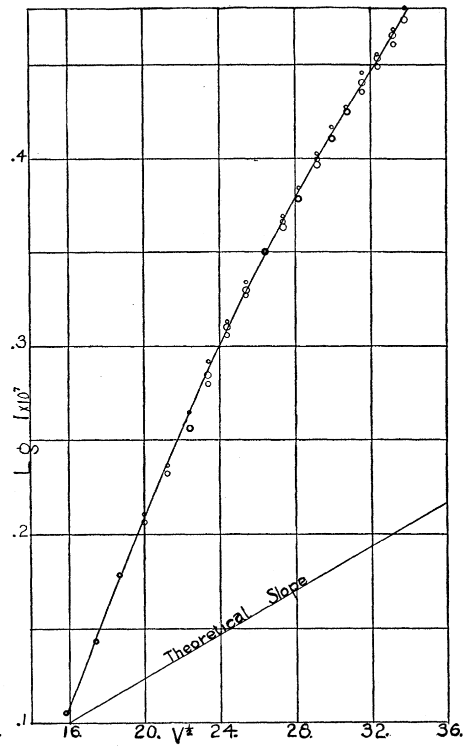

FIG. 4. Schottky curves during second stage for 7 mil filament. Aging has been protracted: 175 hours at 1650 to 1690°K. Data are consistent but curves are not linear and slopes are high.

currents decreased slightly. A curve, typical of this stage is shown in Fig. 4.

A third stage is that in which slopes of the correct value were found as shown in Fig. 5. The attainment of this condition required flashing at a temperature around 1785°K; but the filaments remained in the same condition at lower temperatures as shown in curves 2 and 3 of Fig. 5. In fact, with a filament in this stage the liquid air was removed from the charcoal for several weeks, and after recooling the filament condition was found unchanged. Apparently a requirement necessary for transition to this stage is some evaporation of platinum. It was found that at 1785°K, the filament current remaining constant, the filament diameter decreased sufficiently to cause the temperature to rise an amount sufficient to cause a continuously increasing emission.

A fourth stage appeared when evaporation had continued to such an extent that the slope fell noticeably below the theoretical value as shown in Fig. 6. This decrease appears because (dv/dx_0) entering with an exponent $\frac{1}{2}$ increases the slope more slowly than T decreases it. The seven mil filament used in this case was found after burnout to have a minimum diameter of 5.5 mils. The dotted line in curve 7 shows the slope calculated for this diameter. It will be observed that changes in slope due to decrease in filament diameter are quite small, and are easily distinguishable from the preceding effects.

Discussion of Results

It is difficult and unnecessary to assume a mechanism which will account for the above results. The early, erratic stages seem, however, to indicate the evolution of some volatile material from the filament surface, and the presence of a surface layer of low work function; the emission being increased due to a decreasing thickness of the layer of impurity. The stable

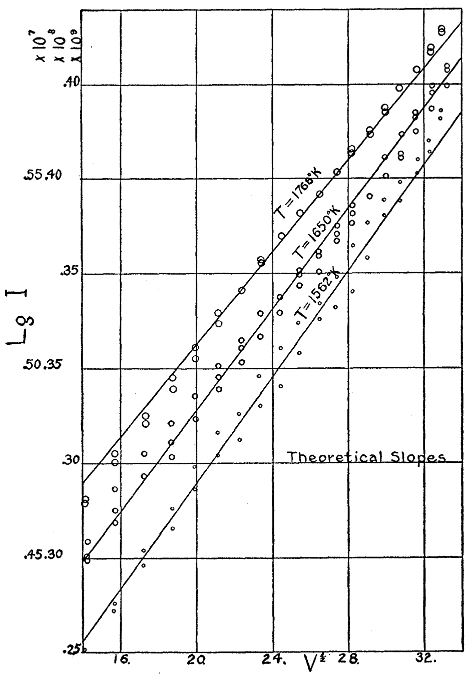

FIG. 5. Schottky curves during third stage for 7 mil filament. Filament has been aged up to 1785°K. Straight lines shown are the theoretical slopes corresponding to the three temperatures.

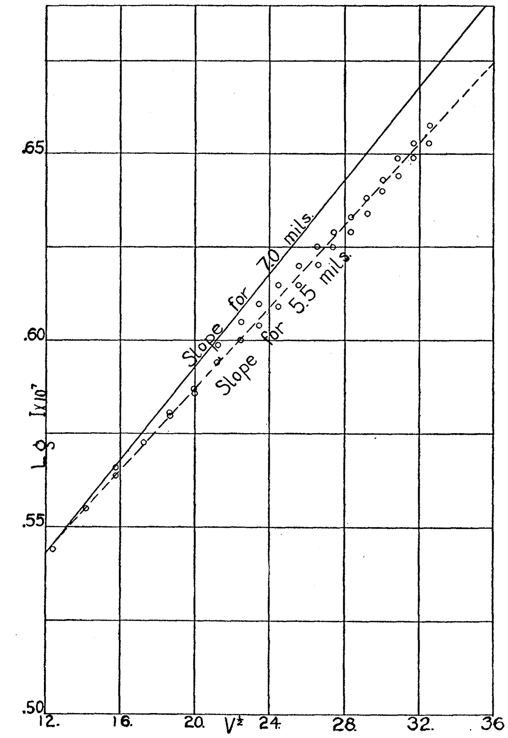

FIG. 6. Schottky curves during fourth stage. Evaporation has occurred so that data fall below the slope calculated for a 7 mil filament but fit slope calculated for 5.5 mil filament; the measured diameter after burnout.

condition yielding high slopes might be attributed to a diffusion of some less volatile material outward to the filament surface. More certainly, evaporation is involved in the transition to the condition in which correct slopes are found. The stability of this condition, then, might point to the previous completion of the process of purification of the interior of the filament by diffusion.

FORCED AGING

Some of the filaments used burned out at low temperatures for reasons which were not apparent. Most of the filaments did not survive long enough to give curves of the correct slope. For this reason, and in order to obtain a more comprehensive view of the phenomena, tests were made in the following fashion: A filament which had been aged at 1755°K for 12 hours was subjected to gradually increasing temperatures for 15 minute intervals. At the end of each 15 minute interval the temperature was reduced to some convenient lower value and thermionic currents measured at anode potentials of 200 and 1250 volts. From these readings the slope of the Schottky curve was computed. The results are shown in Fig. 7. Although the thermionic currents reached an apparently stable value at an aging temperature of about 1917°K the Schottky slopes remained high until a temperature of 1990° was reached. From this point on they decreased rapidly to the theoretical value. The region from 1917 to 1990°K probably corresponds to stage two in previous tests; and is of such a stable character that it seems likely that thermionic and photoelectric work functions would agree. In this way the entire aging process was compressed into 7 hours. The results seem to indicate that the aging temperature is of more importance than the time of aging. The diameters of the filaments were not decreased by evaporation enough to detect with a micrometer after burnout. A filament heated to 2000°K for 30 minutes should[6] decrease in diameter only 0.16

[6] Jones, Langmuir and Mackay, Phys. Rev. 30, 201 (1927).

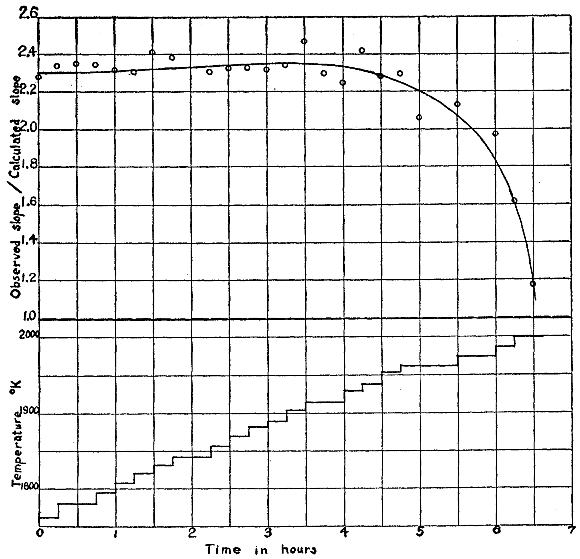

FIG. 7. Diagram showing results of forced aging. Ratio of observed to calculated slopes approaches unity only after aging had progressed to within 45° of the melting point. Slopes were consistent after aging temperatures of 1917°K had been reached.

mil; whereas heated to 1785°K for 175 hours it should decrease 1.6 mils—approximately as found in the longer runs.

CALCULATION OF THERMIONIC CONSTANTS

During the second stage, when the filament condition seemed to be quite stable, although the Schottky slopes were high, values of ϕ and A came out quite high. Because of the lack of straightness of the supersaturation curves it was impossible to determine the slopes of the Richardson curves with accuracy, but the best obtainable values were: $\phi = 7.4$ volts, and $A = 1.3 \times 10^8$ amp./cm²·deg.². These are even higher than those found by DuBridge: $\phi = 6.27$ volts and $A = 1.7 \times 10^4$ amp./cm²·deg.².

The Richardson plots for a filament which had reached the final stage are shown in Fig. 8. The upper curve yields the values $\phi = 5.66 \pm 0.07$ volts and $A = (1.5 \pm 0.7) \times 10^3$ amp./cm²·deg.². The lower curve, taken after further aging, gives $\phi = 5.40 \pm 0.03$ volts and $A = 170 \pm 20$ amp./cm²·deg.². These are probably not the final values since slightly lower values might have been obtained had the filament withstood further treatment. Nevertheless they do indicate that the final values of the constants for pure platinum

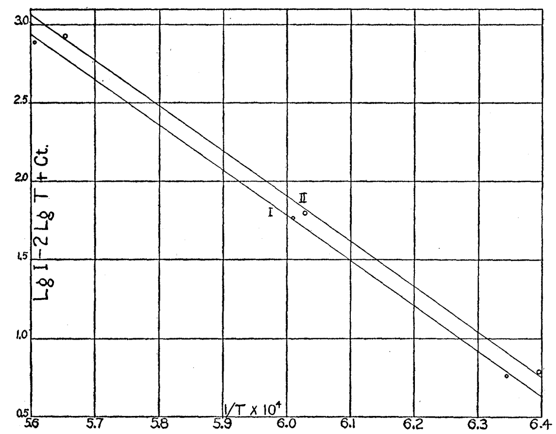

FIG. 8. Richardson curves for two sets of runs each taken at three temperatures. The upper curve gives values of ϕ of 5.66 ± 0.07 volts and $A = (1.5 \pm 0.7) \times 10^3$ amp./cm²·deg.². The lower curve gives $\phi = 5.40 \pm 0.03$ volts and $A = 170 \pm 20$ amp./cm²·deg.².

are considerably lower than those reported by DuBridge, and in particular that the value of A is approaching the theoretical value of 60 amp./cm²·deg.². The above values are subject to some uncertainty because of electrometer fluctuations and the fact that complete data were taken for only three different temperatures. Nevertheless the results are sufficiently consistent that the Richardson slopes can be determined to within about 0.6 percent and the value of A within about 12 percent. Errors due to

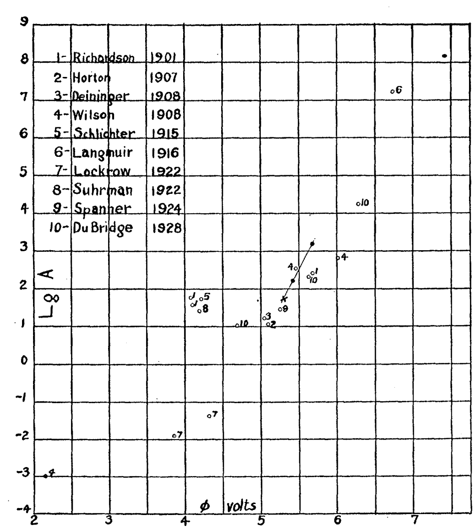

FIG. 9. Compilation of results of several experimenters. Data should give a straight line. X shows probable value of ϕ, 5.29 volts, on the assumption that A should be 60 amp./cm²·deg.².

uncertainty in the calibration of the electrometer and the resistors are certainly less than this.

The high value of A for platinum previously reported has been the cause of some speculation and explanations have been proposed by Fowler[7] and by DuBridge. The present results indicate that this high value is characteristic of a fairly stable but not pure surface condition, and that for a surface cleaned at very high temperatures the value is not far from 60.

Richardson and DuBridge[8] have shown that for a given surface log, A is a linear function of ϕ. The values of these constants for platinum tabulated by Dushman are plotted in Fig. 9. Assuming the straight line as drawn to be correct it is seen that a platinum surface for which $A=60$ should show a work function of about 5.29 volts. Possibly this is close to the true value for clean platinum.

The author wishes to express his appreciation to Dr. W. R. Ham who directed the problem and to Mr. Karl D. Larsen who assisted throughout the work. Assistance was also furnished many times by other members of the Physics Department of The Pennsylvania State College.

[7] Fowler, Proc. Roy. Soc. **A122**, 36 (1929).

[8] Richardson, *Emission of Electricity from Hot Bodies*, p. 135; DuBridge, Proc. Nat. Acad. Sci. **14**, 788 (1928).