THE PHOTOELECTRIC AND THERMIONIC WORK FUNCTIONS OF OUTGASSED PLATINUM

By Lee A. DuBridge*

Abstract

In extending results previously reported the photoelectric and thermionic work functions for platinum were studied while the specimen was put through an extended outgassing process. With monochromatic light the final value of the photoelectric threshold was found to be 1962A (6.30 v.) The thermionic work function increases during outgassing, reaching a final value of 6.35 volts, within 1 percent. The two work functions are thus in agreement within the limits of error. The thermionic constant A of the Richardson T^2 law also increases as the work function increases, reaching a final value which is 200 times or more greater than Dushman's theoretical value of 60.2 amp/cm^2 deg^2.

IN TWO previous articles [1,2] the writer has presented the results of a study of the photoelectric properties of platinum when the surface of the metal is thoroughly cleaned of occluded gases. With light filters to cut out successively the shorter lines in the spectrum of the quartz mercury arc, it was found that the photoelectric threshold for platinum shifted steadily toward the shorter wave-lengths during outgassing, and after prolonged treatment in the highest attainable vacuum reached a final value somewhere between the mercury lines 1943 and 1973A. In extending these results it seemed worth while to determine this limit still more accurately using monochromatic light, and to compare the value of the photoelectric work function so found with the value of the thermionic work function for the same specimen.

Previous attempts to establish the identity of these two quantities for the various metals have succeeded only in the case of tungsten, for which Warner[3] has recently found that after careful outgassing the two work functions are equal within the limits of experimental error. In the case of platinum recent attempts[4] to make a direct comparison of the two "constants" have led to inconclusive results because of the very great difficulties in eliminating the effects of gases. Suhrmann[5] has reported a check between the two, giving 4.6 volts as their common value. However this value for the photoelectric work function (corresponding to a threshold of 2675A) is clearly too low for the outgassed metal in the light of the recent results of Tucker,[6] Woodruff[7] and the author.[2]

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[1] DuBridge, Nat. Acad. Sci. Proc. **12,** 162 (1926).

[2] DuBridge, Phys. Rev. **29,** 451 (1927).

[3] Warner, Nat. Acad. Sci. Proc. **13,** 56 (1927).

[4] Harrison, Phys. Soc. Lon. Proc. **38,** 214 (1926).

[5] Suhrmann, Zeit. f. Physik. **13,** 17 (1923).

[6] Tucker, Phys. Rev. **22,** 574 (1923).

[7] Woodruff, Phys. Rev. **26,** 655 (1925).

A large number of experimental values for the thermionic work function alone for platinum have been reported by various observers, but it is notable that the excellent agreement between results found for metals such as tungsten and molybdenum is completely lacking in the case of platinum. The reported values for this metal are well scattered in the range from 4.0 to 6.6 volts,[8] the range between 5.0 and 5.5 volts being perhaps slightly

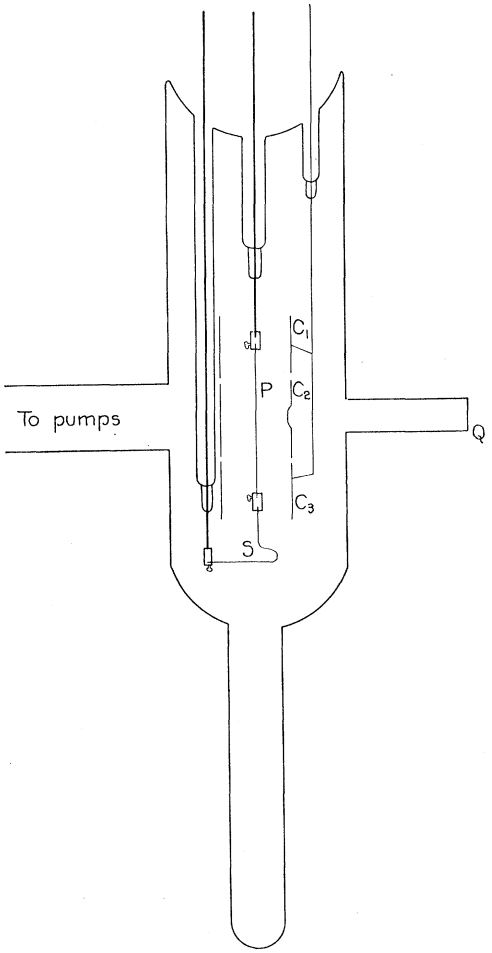

Fig. 1. Tube for study of photoelectric and thermionic properties of Pt.

favored. It has been shown many times that very slight amounts of gas in the surface could produce enormous changes in the thermionic emission, and H. A. Wilson[9] was able to reduce the work function for a platinum specimen to as low as 2.2 volts by heating in an atmosphere of hydrogen. A systematic study of the behavior of the thermionic work function *during*

[8] See Richardson "Emission of Electricity from Hot Bodies" 2nd ed. p. 81.
[9] Wilson, Phil Trans. **208A,** 251 (1908).

the outgassing process seemed therefore desirable in order to determine the limit which this quantity would approach as the thoroughly outgassed state is reached.

Apparatus. The tube used was of the form shown in Fig. 1. The specimen to be tested was a strip of platinum foil, P, 5 cm long, 2 mm wide and about 0.01 mm thick, suspended along the axis of the collecting cylinder C and the coaxial guard ring cylinders C_1 and C_3. The latter cylinders served to collect spurious photoelectric and thermionic currents from the clamps supporting the strip and from the cool ends of the strip itself. The three cylinders were rigidly supported from a pair of Pyrex rods not shown in the diagram. The strip could be heated by an electric current conducted in through heavy tungsten leads. It was kept taut during heating by the weight of the lower clamp, which was a small nickel block attached to the tungsten lead through the flexible copper strip S. The temperature of the platinum was determined with an optical pyrometer focussed through the window Q, correction being made for the transmission of the window and the emissivity of platinum. The temperature scale of Mendenhall[10] was used, though this is in substantial agreement with the more recent one of Worthing[11] in the range of temperature used for the thermionic measurements. The window Q which was of quartz, sealed directly onto a graded quartz to Pyrex seal, served also to admit light from a quartz mercury arc, resolved by a Fuess quartz monochromatic illuminator. The currents to the collecting cylinder were measured by means of a Compton electrometer whose sensitivity at the scale distance used (3 meters) could be brought to 30,000 mm/volt. A series of high resistance shunts was used for measuring the thermionic currents, but the very minute photo-currents were measured by the "rate of charge" method.

The pumps, vacuum conditions and outgassing methods were similar to those used in the previous experiments at the University of Wisconsin. The entire glass system was of Pyrex and all glass on the high vacuum side was thoroughly baked out at temperatures up to 550°C before any measurements were begun. All waxed and greased joints were eliminated from the high vacuum side of the pumps, an important point since much of the previous difficulty in obtaining consistent and reproducible results for platinum can undoubtedly be traced to the presence of organic vapors due to such joints.[12] In one test run made by the writer it was found that sealing off a side tube which contained a wax joint caused an immediate rise in the thermionic work function of the specimen under test from 5.2 to 6.0 volts.

The photoelectric threshold. In order to determine the photoelectric threshold by the usual method the relative intensities of the lines of the mercury spectrum must be known. These were measured for the lines longer than 2200A with a vacuum thermopile and the results checked with those obtained by Kazda[13] for an arc operating under identical conditions.

[10] Mendenhall, Astrophys. J. **33,** 91 (1911).
[11] Worthing, Phys. Rev. **28,** 174 (1926).
[12] This may be the cause of Suhrmann's low value for the work function for *Pt.*
[13] Kazda, Phys. Rev. **26,** 643 (1925).

However the three shortest lines in the spectrum, λ1849, 1943 and 1973A are far too weak to produce a measurable effect on the thermopile, and the previous work had shown that these were just the lines required to determine the threshold for the thoroughly outgassed platinum. Their relative intensities were therefore estimated by the following method. Using a fresh platinum specimen whose threshold was near 2540A the measured photoelectric currents were plotted as a function of the wave-length of the incident light, as read from the drum of the monochromatic illuminator. (Since the drum was originally calibrated only to 2000A it was necessary to shift the prism table and recalibrate the drum to make all lines down to λ1850 available.) The various lines in the mercury spectrum below 2540A then appeared as peaks on this photoelectric curve. Then using the lines for which the relative intensities had been directly measured, the photocurrent per unit intensity was plotted as a function of wave-length. This of course gave a regular curve which could be extrapolated to the shorter wavelengths and the effective intensities of the shorter lines could be deduced, since the photo-currents produced by them had been measured. In making the extrapolation use was made of the following equation for the efficiency of photoelectric emission as a function of frequency recently derived by Uspensky[14] and shown to hold for platinum over a wide range of frequencies.

$$i=(\text{const.}\ /h\nu)\left[(\nu/\nu_0)^{1/2}+(\nu_0/\nu)^{1/2}-2\right].$$

In this equation i represents the photo-current excited by unit intensity of incident light, ν is the frequency of the incident light and ν_0 the threshold frequency. The equation was found to fit the experimental points quite closely and the intensities of the three shortest lines in the spectrum were determined to make their points fall on the curve.

The intensity of λ1849 relative to λ2536 as deduced by this method is approximately 1.8×10^{-5}, and the relative intensities of the three lines, 1849, 1943, and 1973A are in the ratio 1.8:10:13. The computed intensities of these lines *relative to each other* are not much affected by probable errors in extrapolation. All the intensities determined in this manner gave completely consistent results throughout the experiments.

The behavior of the photoelectric threshold during the outgassing of a typical specimen is shown in Fig. 2 in which the photo-current per unit intensity of incident light is plotted as a function of wave-length of the light. Curves I, II, III, and IV represent runs taken at successive stages in the outgassing process. Curve I was taken with a fresh specimen after the initial baking of the tube, and shows a threshold at 2540A. This initial value varied considerably for different specimens. The state represented by curve IV was reached only after 100 hours or more of heating at 1200°–1500°C in the highest attainable vacuum. Continued heating and baking then produced no further change in the curve. When this steady state has been reached—and not before—the photo-currents and the threshold value are

[14] Uspensky, Zeits. f. Physik. **40**, 456 (1926).

perfectly stable and reproducible as long as the vacuum remains unimpaired. Allowing the liquid air around the charcoal tube to run low however causes an immediate rise in the photo-currents and a shift of the threshold toward longer wave-lengths. It is believed that curve IV represents the state of affairs for the most completely outgassed state of the platinum which it is possible to reach by the present method of heat treatment. It will be seen that the threshold for this state is approximately 1962A. This value is in agreement with the previous work with filters and was repeated quite closely for other specimens put through slightly different forms of treatment. It was also repeated for specimens which had been put through a complete series of thermionic measurements as described in the next section. *The*

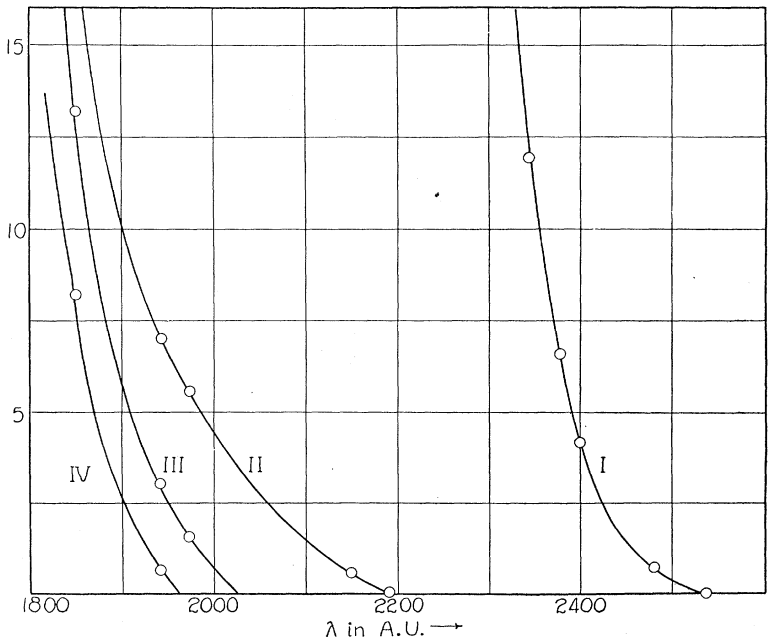

Fig. 2. Photoelectric curves for Pt during successive stages of outgassing.

photoelectric work function for outgassed platinum is therefore 6.30 volts, with a probable error of not more than 0.5 percent. This value may of course be slightly further reduced when better vacuum conditions and outgassing methods become available.

The thermionic work function. A study of the behavior of the thermionic work function during outgassing showed at once that the thermionic currents were even more sensitive to slight traces of gas than were the photo-currents. Thus with the tubes connected to the pumps it was found nearly impossible to reach a state where consistent reproducible values of the work function could be obtained. The *average* values obtained showed a consistent increase during outgassing from about 4.6 volts for a fresh specimen after a thorough

initial baking to something over 6.0 volts after prolonged heating. The deviations from the mean value were however sometimes as great as 50 percent for a fresh specimen, though they could be reduced to 5 percent after long treatment.

After burning out several strips in unsuccessful attempts to bring them to a more steady state by more intense heating, the tube was finally arranged so that it could be sealed from the pumps and a small amount of magnesium vaporized in the lower part to act as a "getter." After a few hours of heating under these conditions (after 100 hours or more of heating before sealing off) and with the charcoal tube immersed in liquid air, the erratic behavior soon ceased and consistent values of the emission and the work function could be

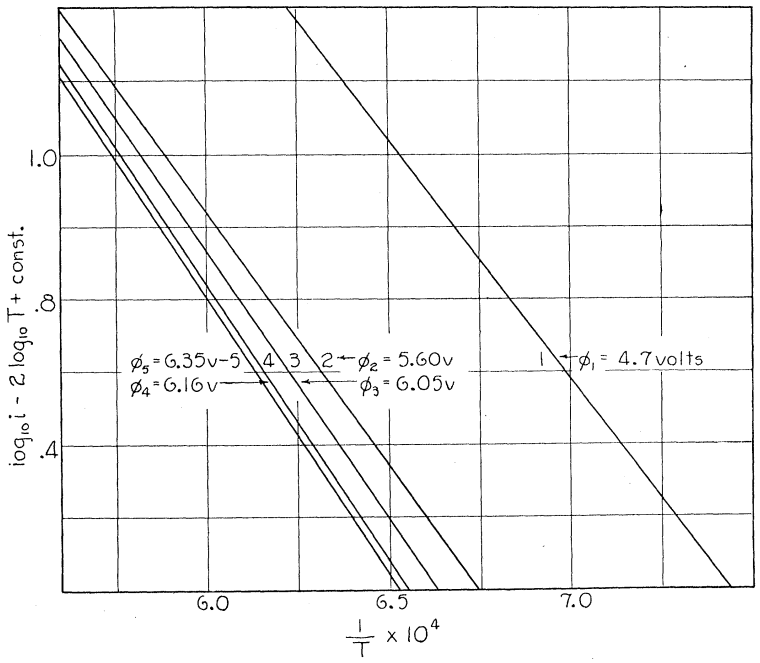

Fig. 3. Thermionic curves for Pt during successive stages of outgassing.

obtained. The behavior of a typical specimen during outgassing is shown in Fig. 3 in which the usual "Richardson straight lines" are plotted for successive stages in the outgassing process. The slopes of these lines are proportional to the work function b of Richardson's T^2 law. Curve 5 is the final one obtained after sealing off the tube. The photoelectric curve for this same specimen, after sealing off, coincided with curve IV of Fig. 2. It will be seen that the final value of the thermionic work function, 6.35 volts, is in remarkably good agreement with the photoelectric value. This final value varied somewhat from specimen to specimen but never differed by more than 0.1 volt from the above value. The error due to the uncertainty in the temperature scale may be as large as this. *The agreement between the photo-*

electric and thermionic work functions for outgassed platinum is thus established, within the limits of error.

Two points in connection with the thermionic emission from partially outgassed specimens may be of interest. In the first place the thermionic straight lines for such specimens sometimes showed abnormally large slopes, corresponding to work functions as high as 7.0 volts. It was found that this was due to a progressive change in the sensitivity of the specimen during the time the run was in progress, and was not a real characteristic of the platinum. This is mentioned merely to indicate that values of ϕ_0 higher than 6.35 volts which have been reported by other observers[7,15] are not necessarily indications that a more completely outgassed state of the platinum had been reached than was attained in the present work.

In the second place it was found that the thermionic emission from fresh platinum specimen was in many ways analogous in its behavior to that from thoriated tungsten filaments. This suggests that perhaps the same sort of diffusion and evaporation process is taking place in the two cases, and it is natural to assume that the hydrogen absorbed in the platinum plays the role of the thoria in the tungsten. Many peculiar effects in the behavior of both photoelectric and thermionic currents from partially outgassed specimens can be interpreted on the basis of this analogy.

The thermionic constant A. As a result of the simple geometrical arrangement of the emitting surface and collecting cylinder in the present experiments it was possible to compute the absolute value of the thermionic current per unit area of emitting surface with reasonable accuracy and thus to determine the constant A in the Richardson T^2 law. Richardson and Dushman[17] have suggested that A should be a universal constant for clean metals having the value 60.2 amp/cm^2 deg^2. Dushman[18] has confirmed this value (roughly at least, since very accurate determinations of A are nearly impossible) for the case of tungsten, tantalum and molybdenum. On computing the value of A from carefully taken emission data on several outgassed platinum specimens in the present work however, values 200 times or more as great as the theoretical value were obtained. Fresh specimens on the other hand gave values of A considerably too low. In fact there is a very definite increase in A accompanying the increase in b or ϕ_0 which takes place during outgassing. This increase in A becomes more rapid as outgassing proceeds and on plotting it was found that log A is roughly proportional to b. In one particular case as ϕ_0 for a specimen increased from 4.7 to 6.4 volts during outgassing the corresponding values of A increased from 11.5 to 14,000. Moreover the values of A and b obtained by other observers for platinum show this same behavior, a fact which has been mentioned by Richardson[16] and by H. A. Wilson.[9] This is clearly shown in the following

[15] Langmuir, Phys. Rev. **2**, 450 (1913).
[16] Richardson, "Emission of Elect. etc" p. 137.
[17] Dushman, Phys. Rev. **21**, 623 (1923).
[18] Dushman, Phys. Rev. **25**, 338 (1925).

table in which are collected values of A and b and ϕ_0 obtained by various observers along with some of the values obtained in the present work. As would be expected the individual values of A are somewhat scattered but the general trend is unmistakable.

The values of A found by the author for thoroughly outgassed specimens when conditions were at their best ran consistently between 10,000 and 20,000. The order of magnitude of A for cleaned Pt is thus definitely greater than that required by Dushman's theory.

TABLE I

Concurrent variations of thermionic constants.

Author	b(deg K)	ϕ_0(volts)	A(amp/cm^2 deg^2)
Wilson[9]	25,600	2.18	10.7×10^{-4}
Richardson[8]	47,500	4.10	39.8
Du Bridge	54,500	4.69	11.5
Deininger[19]	58,500	5.02	16.2
Wilson[9]	63,000	5.45	366.
DuBridge	65,000	5.60	235.
Richardson[8]	65,500	5.65	265.
Wilson[9]	70,000	6.00	620.
DuBridge	72,000	6.20	6450.
"	73,000	6.30	8130.
"	74,200	6.40	14000.
Langmuir[15]	77,000	6.62	$107.\times10^6$

The relation between A and b shown in Table I has also been found for other metals. Thus Kingdon[20] found that if a clean tungsten surface is coated with oxygen the work function of the surface increases from 4.5 to 9.2 volts and at the same time the value of A increases from 60 to 5×10^{11}. Coating a tungsten surface with thoria reduced the value of ϕ_0 to 2.68 volts and A to approximately 7, while coating with caesium reduced ϕ_0 to 0.715 volt and A to 10^{-3} amp/cm^2 deg^2. It thus appears that this direct connection between A and b may be quite general, applying to all surfaces, and that Dushman's value of A is obtained experimentally only for those surfaces for which ϕ_0 happens to have the value characteristic of clean tungsten or molybdenum, namely 4.5 volts. Further investigation of this point seems desirable.

The author is greatly indebted to Professor Millikan and the staff of the Norman Bridge Laboratory for the facilities placed at his disposal.

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[19] Deininger, Ann. d. Physik. **25,** 285 (1908).
[20] Kingdon, Phys. Rev. **24,** 510 (1924).