EFFECT OF HEAT TREATMENT ON THE PHOTO-ELECTRIC EMISSION FROM PLATINUM

By F. G. Tucker

Abstract

Effect of heat treatment on the photo-electric emission from platinum. A thin Pt foil was mounted between heavy leads inside a Faraday cylinder in a pyrex tube with a quartz window sealed to it by means of a graded seal. The *threshold* or long wave-length limit λ_0 was determined by plotting the current per unit light intensity as a function of wave-length of the Hg arc line used. This threshold was found to vary with the previous heat treatment. Glowing the foil at 900°C for 8 hours gave repeatedly a value close to 2700 A; glowing for 4 or 5 hours at bright yellow heat decreased the emission greatly and shifted λ_0 to 2475 A. Immediately after glowing for 2 hours at a temperature of over 1400°C, the emission from the suddenly cooled foil was found to be zero even under the influence of the full radiation of the Hg arc; after 5 minutes the photo-emission began to appear and increased rapidly at first and then more slowly. Evidently the threshold for pure gas-free Pt must be below 1849 A and the effects ordinarily observed must be due to a gas film or some other film formed on the surface. This is also suggested by the shift of λ_0 to a longer wave-length, 2770 A, when the tube was baked at 200°C without glowing the foil.

Variation of photo-electric threshold for platinum with temperature to 600°C.—After a given moderate heat treatment of the foil, the threshold was found to be the same at 600° as at 20°. This indicates that the film responsible for the emission was unchanged and that the threshold under these conditions does not depend on the kinetic energy of the free electrons in the foil.

Introduction

THE recent work of Millikan[1] on the relation existing between the photo-electric limiting frequencies of two elements and their contact difference of potential has led to the very important conclusion that either the electrons emitted under the influence of light are free electrons, or the electron is able to escape from the atom with energy $h\nu$, where h is Planck's constant and ν is the frequency of the incident light. The present investigation grew out of an attempt to obtain additional evidence on the nature of photo-electrons, by studying the temperature variation of the photo-electric threshold of platinum which had been denuded of gases by glowing at high temperatures.

[1] Millikan, Phys. Rev. (2) **18**, 236, 1921

Apparatus and Procedure

The mounting of the emitting filament is shown in Fig. 1 and is essentially the same as used by Koppius[2] in his recent determination of the long wave-length limit of platinum. The filament F of platinum foil, 20 mm long, 5 mm wide and .0005 inch thick, is clamped and riveted to the copper jaws BB'. The leads AA' are 1/8 inch tungsten rods driven into holes bored in the jaws BB' and sealed directly into pyrex glass. C represents a copper-oxide Faraday cylinder which served to catch the emitted electrons. The cylinder wall is not perforated, but the hole O allows the incident radiation to fall upon the filament. Connection is made to the measuring electrometer by means of two tungsten wires, similar to E, which also support the cylinder.

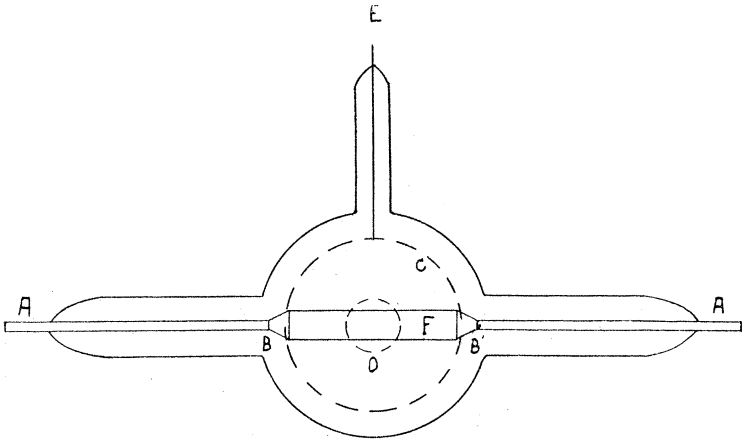

Fig. 1. Photo-electric tube.

In the original apparatus, the end of the pyrex tube, 40 mm in diameter, was closed with a quartz window cemented to the glass with a special cement kindly furnished by the Mantle Lamp Company of America. This joint was repeatedly baked for hours at 200°–225°C without impairing in the least the vacuum in the system. This tube was later replaced by a similar one built by the Cooper-Hewitt Electric Company, in which a window of clear fused quartz was sealed to a quartz tube 40 mm in diameter and about 2 cm long. By means of a graded seal[3] this quartz tube was in turn sealed to a pyrex one of the same diameter, and the emitting filament was mounted as before. This tube was baked at 450°C. The system was exhausted by a mercury diffusion pump working against an x-ray fore-vacuum produced by a Gaede rotary

[2] Koppius, Phys. Rev. (2) **18**, 443, 1921

[3] Engineering Dept. Bull. No. 104, Cooper-Hewitt Electric Co.

mercury pump. Pressures were measured with a Buckley ionization manometer[4] and the usual liquid air traps were inserted in the system to prevent the mercury vapor from diffusing over into the ionization gauge and the part of the tube containing the filament. The pumps were run continuously while the filament was being glowed and while measurements of photo-currents were being taken. In every case the manometer indicated a pressure between 1 and 10×10^{-6} mm of mercury.

A Cooper-Hewitt quartz mercury arc served as a source of illumination and monochromatic radiation of a desired wave-length was directed upon the filament by means of a Hilger monochromator. In order to test the purity of the lines resolved by this instrument, the emergent light was photographed with a large quartz spectrograph. For the principal mercury lines below λ2800, with the single exception of λ2650, the plates showed that only the line corresponding to the reading of the wave-length drum of the illuminator was transmitted. In the case of λ2650 there was a faint transmission of the line λ2640.

To determine the long wave-length limit, the photo-currents per unit intensity of the incident light were plotted as ordinates against wave-lengths as abscissas. The intercept of this curve upon the wave-length axis gave the limiting wave-length, and results by this method have been shown to agree, within the limits of experimental error, with the direct method of stopping potentials.[5] The relative intensities of the lines used for illuminating the target were measured by means of a sensitive thermopile and Coblentz galvanometer.[6] The results of these measurements are given in Table I.

TABLE I

Wave-length	Average galvanometer deflection
2800 A	4.9
2650	9.0
2536	11.7
2483	3.1
2400	1.5
2378	1.0
2300	.6

Before taking observations the tube was baked for five or six hours, at 200°C in the one case and at 450°C in the other. The filament was then glowed at various temperatures ranging from bright red to white heat, as indicated under results. The Faraday cylinder was main-

[4] Buckley, Proc. Nat. Acad. Sci. **2**, 683, 1916
[5] Millikan, Phys. Rev. (2) **7**, 355, 1916
[6] Souder, Phys. Rev. (2) **8**, 310, 1916;
Coblentz, Bull. Bur. Stds. **9**, 56, 1913

tained at a positive potential of 15 to 50 volts with respect to the filament and the photo-currents were measured with a quadrant electrometer having a sensibility of 1600 mm per volt. The quartz arc was mounted in an asbestos lined box and run at a high temperature as the work of Souder[6] showed that the radiant energy output was constant under these conditions. Throughout the experiments it was run at 117 volts and 2.72 amperes. A change of three per cent in the arc voltage could be readily detected in the photo-current.

Experimental Results

In each case the initial behavior of the filament was similar to that observed by Koppius,[2] viz., no appreciable emission could be obtained until after the filament had been glowed a few minutes at red heat. After a preliminary glowing at bright red heat for 8 hours, the long wave-length limit of the filament fell consistently at about 2700 A, as shown in Curve I, Fig. 2. The photo-currents varied from day to day but the

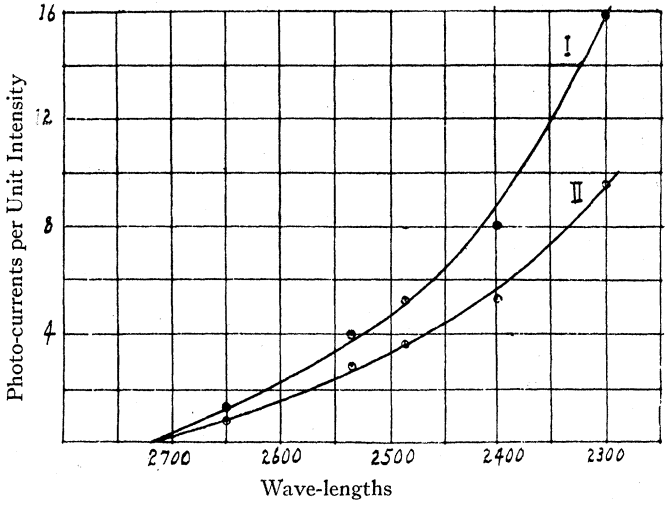

Fig. 2

threshold frequency remained practically constant as long as the filament was subjected to this particular type of preliminary heat treatment.

When the glowing temperature was increased, however, the value of λ_0 was shifted toward the shorter wave-lengths. Curve I, Fig. 3, is a typical example of the results obtained after heating the foil four or five hours at bright yellow heat. The emission had decreased to such an extent that it was necessary to double the slit width of the illuminator in order to get currents which would be accurately measured. The inter-

cept of Curve I gives a value of 2475 A for the long wave-length limit instead of approximately 2700 A which had been obtained consistently in previous observations. Allowing the filament to stand in a vacuum of 1×10^{-5} mm for 24 or 48 hours produced a large increase in the photo-current but the long wave-length limit was displaced only about 25 A.

In an endeavor to find the cause for the change in behavior of the filament, after obtaining the results shown in Curve I, Fig. 3, the tube was baked for three hours at 200°C and readings were taken without glowing the filament. These observations are shown in Curve II, Fig. 3. The photo-currents for the shorter wave-lengths were increased to ap-

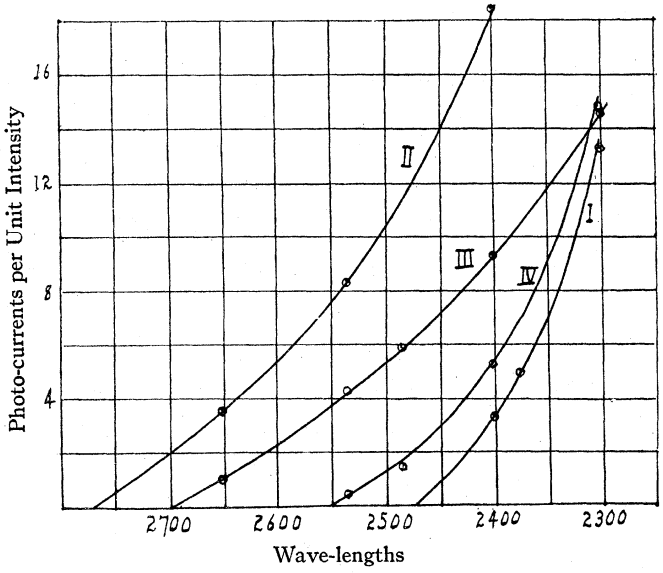

Fig. 3

proximately nine times the values obtained before the baking of the tube, and the intercept was shifted to 2770 A. After glowing the filament for 30 minutes at red heat Curve III was obtained which is practically identical with results obtained in the earlier part of the work. Glowing the foil another 30 minutes at white heat shifted the observations to those shown in Curve IV.

It is evident from these results that the gases given off by the copper-oxide cylinder during the baking out of the tube and the glowing of the filament, have a pronounced effect upon the photo-emission, and the value of the limiting frequency. Heating at temperatures of 800°–900°C is not sufficient to denude the foil of gases. Even after glowing at white heat the filament is very quickly covered with a film of gas sufficient to affect the electron emission. This was shown by the following experi-

ment. The filament was glowed several hours at white heat and then allowed to cool to room temperature, and immediately before taking an observation it was again glowed at white heat for 30 seconds. When illuminated with the line λ2300 there was no measurable electron emission, even after the slit of the monochromator had been opened to a width of 2.5 mm, which was four times the width regularly used. After an interval of three minutes the same illumination gave a deflection of 5 mm in 40 seconds and after five hours the deflection had risen to 100 mm. Another glowing for five minutes at white heat reduced the deflection to 1 mm.

In the earlier experiments with the improved tube, the results obtained with the first filament were verified. However, after the new filament had been subjected to several six hour glowings at bright yellow heat,

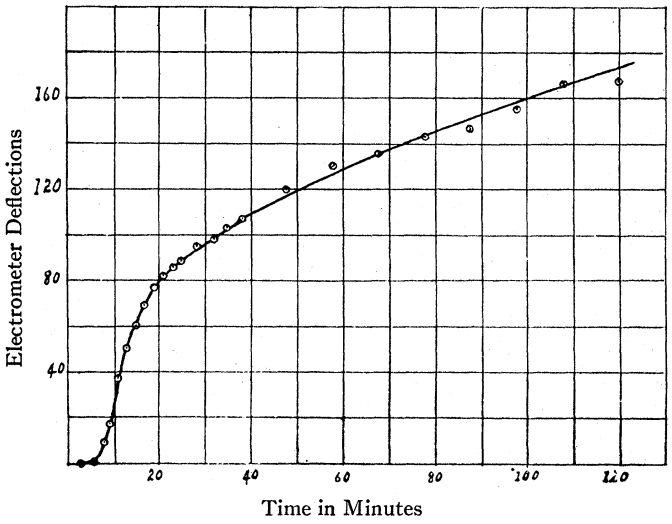

Fig. 4

it showed no emission under the influence of the radiation transmitted by the monochromator, even for wave-lengths down to 2000 A and with a slit width of 3.8 mm. The full light of the arc was then focused directly upon the filament and a moderately large emission was obtained.

A more careful study of the photo-current obtained under the influence of the unresolved light of the mercury arc revealed the following facts. After repeated glowings at bright yellow heat this emission persisted and showed a decided increase with time after glowing. When a five hour glowing at bright yellow heat was followed by heating the filament for two hours at a black body temperature of 1510°K, the photo-emission was practically zero for a few minutes after the heating current was stopped. Following this the emission increased, rapidly at first,

and then more slowly. A typical recovery curve is shown in Fig. 4 in which the ordinates are electrometer deflections in 40 seconds. After allowing the filament to recover for two hours another glowing at the same temperature caused it to reproduce the behavior shown in Fig. 4.

The temperature of the white hot filament was measured with an optical pyrometer, and since this instrument was sighted through the quartz window upon the bright platinum surface, the true temperature of the filament was approximately 150°–200°C[7] higher than the pyrometer reading. The true temperature of the filament, therefore, was approximately 1450°C.

In the earlier part of the investigation the threshold of platinum at a temperature of 600°C was determined. The observations shown in Curve II, Fig. 1 were taken immediately after those represented by Curve I. It is evident that the long wave-length limit is not shifted when the temperature of the foil is increased from 20°C to 600°C, although the photo-currents are decreased.

Discussion

From these observations it is evident that glowing at bright red or even yellow heat produces only a slight change in the gaseous layer upon platinum foil. The later experiments show that a temperature of approximately 1450°C is necessary to remove this film, or at any rate to modify it in such a manner that the surface is no longer photo-sensitive for radiation from a quartz mercury arc. We are led, therefore, to the conclusion that when a platinum surface is most free from gases (perhaps it can never be completely free) it exhibits no photo-electric emission for wave-lengths greater than 1849 A.[8] Sende and Simon[9] and also Suhrmann,[10] working in Hallwach's laboratory have recently arrived at the same conclusion concerning the photo-electric threshold of platinum.[11] Several earlier investigators,[12] on the other hand, working under less favorable conditions for denuding the foil of gases, have arrived at different conclusions.

The view that the intrinsic long wave-length limit of platinum is less than 1849 A receives additional support from the work of Kustner,[13]

[7] Bureau Standards Technical Paper No. 170, p. 113, 1921

[8] Hughes, Report on Photo-Electricity. Bull. Nat. Research Council **2**, 125, 1921

[9] Sende and Simon, Ann. der Phys. **65**, 697, 1921

[10] Suhrmann, Ann. der Phys. **67**, 43, 1922

[11] Since this was written an article has appeared by Welo, Phil. Mag. **45**, 593, 1923, in which the author concludes that gas free platinum is photo-sensitive for wave-lengths longer than 1849 A.

[12] Piersol, Phys. Rev. **8**, 238, 1916, gives detailed bibliography of earlier work

[13] Kustner, Ann. der Phys. **46**, 893, 1915

who found that newly distilled zinc showed no photo-emission under the influence of a quartz mercury arc. Further evidence is also furnished by Hughes'[14] study of the contact potential of zinc. This author found newly distilled zinc to be electro-negative to platinum but upon exposure to a trace of reacting gas it became electro-positive. In view of the relation existing between the photoelectric threshold of two elements and their contact difference of potential,[15] the results obtained by Hughes indicate that λ_0 for zinc is shifted toward the violet as the surface is denuded of gases.

At first sight this shift in the limiting frequency of platinum after glowing at high temperatures seems to destroy the numerical relationship,[15, 16] which has been shown to exist between the work function φ_0 for thermionic emission, and the function $h\nu_0$ for photo-electric emission. If, however, we substitute in the equation

$$eV = h\nu_0 = hc/\lambda_0.$$

$e = 4.77 \times 10^{-10}$; $h = 6.55 \times 10^{-27}$; $c = 3.00 \times 10^{10}$; and $\lambda_0 = 1850$ A, we find a value for V of 6.68 volts, while Langmuir[17] has obtained a value of 6.62 volts for ϕ_0 for platinum under very good conditions as to freedom from gases. Richardson,[18] on the other hand, is inclined to consider approximately 5.00 volts as the "best guess" for the thermionic work function of platinum.

The fact that after a moderate heat treatment of the foil, the threshold was found to be the same at 600°C as at 20°C does not enable us to draw any conclusions concerning the nature of photo-electrons. It can only be interpreted as indicating that the film responsible for the emission was not changed; and if the threshold is a function of the kinetic energy of the free electrons in the metal, the fact was completely masked by the much greater effect due to the surface film.

I take this occasion to express my appreciation to Professor Millikan for suggesting this problem and for his continued interest in the work, and to Professors Gale and Dempster for their many helpful suggestions, especially during the latter part of the investigation.

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[14] Hughes, Phil. Mag. **28**, 337, 1914
[15] Millikan, Phys. Rev. **18**, 242, 1921
[16] Richardson, Science N. S. **54**, 283, 1921
[17] Richardson, Emission of Electricity from Hot Bodies, Second Edition, p. 81, 1921.
[18] Richardson, Ibid. p. 87
[19] Received May 22, 1923—Ed.