THE THERMIONIC EMISSION FROM CLEAN PLATINUM

By Lee A. DuBridge[1]

Abstract

The thermionic emission from thoroughly outgassed platinum in high vacuum has been measured to one-half percent over the temperature range 1360 to 1750°K, the temperatures being measured by careful optical pyrometry. The values obtained for the thermionic constants of the T^2 law are, when corrected for the Schottky effect, $b=72{,}820$°K, $\phi=6.27$ volts, $A=17{,}000$ amp/cm^2 deg^2. The value of ϕ is possibly in error by not more than 1 percent because of uncertainties in the temperature scale, and agrees within one-half percent with the value of the photoelectric work function previously obtained. The data confirm the previous announcement that for clean platinum A is 250 times greater than the theoretical value of 60.2 amp/cm^2 deg^2.

ALTHOUGH practically the first and for many years almost the only metal whose thermionic and photoelectric behavior was extensively studied, platinum has so completely failed to yield consistent results that the most careful existing measurements of the surface work function differ among themselves by as much as nearly 2 volts. It was early recognized through the work by Wilson,[2] Richardson,[3] Hallwachs[4] and many others that the cause of the discrepancies in both the photoelectric and thermionic work was to be found in the extraordinary tenacity with which the surface clung to slight traces of gas which greatly affected its electron emission. The work of many observers showed that as the surface was denuded of gases the work function steadily increased. In 1927 the writer[5] showed that by employing modern high vacuum technique and extending the time of outgassing of the metal to the order of one hundred hours a steady state could be reached in which both the photoelectric and thermionic work functions showed consistently a common value of approximately 6.3 volts. Pressure measurements indicated that this value was characteristic of a nearly gas-free surface. Clean platinum was thus established as the most electro-negative of any of the metals so far studied,—a fact not inconsistent with its position at the extreme right of the periodic table.

In addition, measurements of the constant A of the equation $I=AT^2e^{-b/T}$ yielded values 230 times greater than the theoretical value of 60.2 observed[6] for other metals. The possible significance of this result has been discussed elsewhere.[7] However in order to place the above values for the thermionic constants on a more exact quantitative basis it was necessary to extend the

[1] National Research Fellow.
[2] Wilson, Phil. Trans. **208A**, 251 (1908).
[3] Richardson, Emission of Electricity from Hot Bodies, Chap. IV.
[4] Wiedmann and Hallwachs, Verh. Deut. Phys. Ges. **16**, 107 (1914).
[5] DuBridge, Phys. Rev. **29**, 451 (1927); **31**, 236 (1928).
[6] Dushman, Phys. Rev. **21**, 623 (1923); **25**, 338 (1925).
[7] DuBridge, Proc. Nat. Acad. 14,788 (Oct., 1928).

previous measurement to a greater precision and a greater range of temperatures and currents. The present paper is a report of this work.

Apparatus and Methods

A diagram of the thermionic tube used is shown in Fig. 1. It was not essentially different from that used in the previous measurements,[5] except that the charcoal trap was replaced by an ionization gauge in which magnesium could be vaporized, and which served to measure the pressure and also to assist with the clean-up of the residual gases after the tube was sealed from the pumps. The filament of the present tube was mounted as shown so as to be more easily replaceable. It consisted of a platinum strip $2\times60\times0.01$ mm suspended along the axis of three coaxial nickel cylinders, the two outer ones acting as guard rings. The length of the central collecting cylinder, measured from center to center of the slits separating it from the guard rings, was 3.4 cm, so that the platinum surface from which emission was received was approximately 1.36 sq. cm. Connection of this cylinder to the electrometer was made through a well insulated seal coming directly out through the side of the tube in a direction at right angles to the plane of the figure.

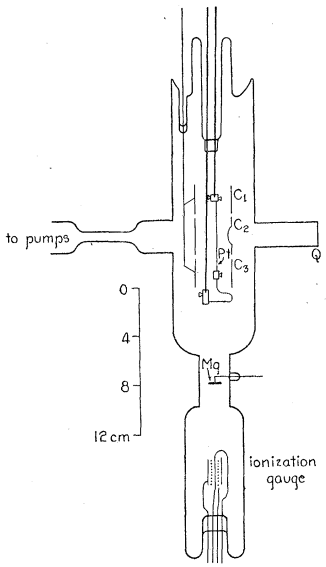

Fig. 1. Diagram of thermionic tube.

Outgassing process. After the installation of each new platinum specimen the whole tube was baked at 450–500°C for from 6 to 15 hours. The nickel cylinders were then heated to about 1300°C by high frequency induction until they no longer gave off appreciable amounts of gas. The grid and plate of the ionization gauge were given a thorough outgassing by bombardment. The whole tube was then rebaked for usually 24 hours and the cylinders again heated. During this time the platinum strip was kept glowing continuously at about 1300°C. After the above treatment the filament was kept at this temperature, with frequent periods at higher temperatures up to 1500°C, until the pressure as read by the ionization gauge was of the order of 10^{-8} mm with the strip hot, or until the thermionic emission from the platinum became nearly constant. The work function at this stage was usually about 6.0 volts. The magnesium disk was then heated by induction (having previously been outgassed) until a considerable quantity was vaporized throughout the tube; the tube was then carefully sealed off.* After several hours of heating of the strip with the ionization-gauge filament running at an emission of 10 milliamps. at 100 volts, the emission from the platinum reached a steady state and final measurements could then be taken.

It should be mentioned that only a small percentage of the platinum specimens installed survived the complete treatment. Some developed hot

* The author is indebted to Dr. J. A. Becker of the Bell Telephone Laboratories for helpful suggestions as to vacuum technique.

spots and soon melted at these points. A greater number simply broke for no apparent reason while at temperatures 400° below the melting point. This is probably caused by the recrystallization of platinum known to take place during long heating. The breaks occur even when the tension used to keep the filament straight is scarcely greater than the weight of the filament itself. However the occasional filaments which did withstand the outgassing process gave a beautifully consistent and reproducible emission.

Temperature measurements. The temperature of the platinum was measured by a Leeds & Northrup optical pyrometer focussed through the window *Q* whose absorption was known. The pyrometer was calibrated originally by the Bureau of Standards and was twice recalibrated in this laboratory by Dr. A. H. Warner and the author against a standard tungsten lamp which had been supplied to Dr. C. H. Prescott for his work[8] at this institute by Dr. Forsythe of the Nela Laboratories. All three calibrations were in agreement within 2° over the whole range.

The procedure in taking a run was at each successive value of the filament heating current to take simultaneous measurements of the temperature and thermionic emission,—making for each temperature measurement from six to twelve pyrometer settings. The measured temperatures, after being corrected for the emissivity of the platinum and the absorption of the window, were then plotted on a large sheet of graph paper as a function of the heating current. A smooth curve was drawn through the points, none of which fell off the curve by more than two degrees. The final temperatures were read from this curve and were therefore consistent among themselves for each run to better than one degree.

The emissivity of well-aged platinum as a function of temperature has recently been carefully measured by Worthing,[9] and his temperature scale was employed in the present work. It differs slightly from the earlier scale of Waidner and Burgess[10] and Mendenhall.[11] If the latter scale is used values of the work function are obtained which are about 1 percent lower than those given below. The discrepancy between the two scales is found particularly at the higher temperatures and Worthing gives evidence to indicate that considerable confidence may be placed in his measurements at these temperatures. However, as he himself says, the data for platinum are not completely satisfactory and this constitutes the chief source of error in the present experiments.

Emission measurements. Because of the high work function of platinum and the necessity of working at temperatures below 1750°K the emission currents were for the most part beyond the range of galvanometer measurements. Consequently a Compton electrometer shunted by a high resistance was used. Four such resistances were employed to enable a large range of currents (10^5 to 1) to be measured. They were mounted within the electrometer cage so that any one could be easily switched in by means of mercury

[8] Prescott and Hincke, Phys. Rev. **31,** 130 (1928).
[9] Worthing, Phys. Rev., **28,** 174 (1926).
[10] Waidner and Burgess, Bull. Bur. Standards, **3,** 163 (1907).
[11] Mendenhall, Astrophys. J., **33,** 91 (1911).

switches operated from outside. The three highest resistances were of India ink on drawing paper sealed in a tube of paraffin. The lowest was simply a metallic grid leak. Their values as determined by the time of leak across a standard condenser were 13,400, 1342, 68.8 and 2.58 megohms. The ratios between the successive resistances could also be accurately checked by measuring with them the same thermionic current. The need for more resistances of intermediate values was rendered unnecessary by the use of a null method of measuring. One end of the resistance in use was connected to the insulated quadrants and the other through a resistance box potentiometer to ground. The other electrometer quadrants were earthed directly. By means of the potentiometer the electrometer deflection could be brought to zero for each measurement, the potential required for this being of course just equal to the drop across the resistance due to the current being measured. The potentiometer readings in volts divided by the value of the resistance in ohms gave directly the thermionic current in amperes. By this means currents varying by a factor of nearly 500 could be easily measured with a single resistance. The potentials actually used varied from 0.01 to 1.0 volt and with the electrometer sensitivity used these could be determined to about 1/5000 volts, which is 2 percent of the smaller and 0.02 percent of the higher potential. However the smaller readings for each resistance were repeated with the next higher resistance with increased accuracy. On the other hand the slight unsteadiness in the filament heating current limited the accuracy of the higher potential measurements to about 0.1 percent so that on the whole the potentiometer readings were consistent to better than one-half percent. The errors in the measurements of the resistances themselves were also of about this order of magnitude.

To obtain the above degree of steadiness (0.1 percent) in the thermionic currents the heating current through the strip had to be kept constant to 1 part in 5000. This was accomplished by using two 20-volt banks of large storage cells in parallel and a series of fixed constantan resistances which could be easily switched in and out, all shunted by a good high resistance rheostat for fine adjustment. The current passed through a 0.1 ohm standard resistance and was measured by a potentiometer and standard cell. The resistances were so arranged that by proper manipulation the heating current could be set and maintained at any desired value within the limits required. It was kept at each value for several minutes before readings were taken to insure complete thermal equilibrium.

Schottky effect. In order to correct the values of b and A for the effect of the accelerating potential, V, between the filament and cylinders the Schottky equation was used. This may be written,

$$\Delta b = 2.303 T(d \log_{10} I/dV^{1/2})V^{1/2}.$$

The value of the derivative is obtained by plotting the logarithm of the thermionic current as a function of the square root of the potential V, and determining the slope of the resulting straight line. Such a plot for a temperature of 1618°K is shown in Fig. 2. From this we calculate, $\Delta b = 370$°K approximately, for $V = 132$ volts, the value used in the measurements given below. This is in good agreement with the values obtained for other temperatures.

Results

As is usual in such measurements the value of the work function was determined from the slope of the straight line obtained by plotting (log I/T^2) as a function of $1/T$. The value of b so obtained is then used to calculate log A for each reading. The constancy of the values of A obtained for various temperatures is a test of the consistency of the emission and temperature readings. The measurements and calculations for one of the best runs obtained are summarized in Table I and Fig. 3. The first three columns of the table give, respectively, the filament heating current, the emission current reduced to amp/cm², and the true temperature of the strip. The next two columns give data used in plotting the curve. The sixth column gives the calculated values of $b/2.3T$, using for b the slope of the curve of Fig. 3. The last column gives the values of log A obtained by adding the values in column 6 to the corresponding values in column 4. It will be noted that the measurements extend over a range of temperature of nearly 400° which is about the maximum that can be conveniently obtained for platinum, and that the values of the emission current vary over a factor of over 10^5.

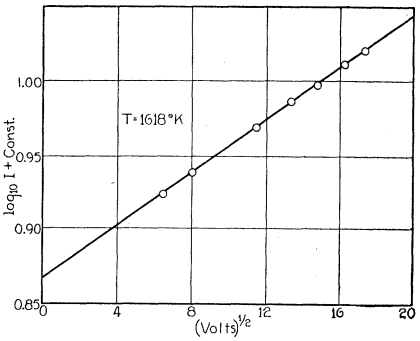

Fig. 2. The Schottky effect.

Table I. *Thermionic Emission data for Pt.*

b (from slope) = 72,450°K. V = 132 Volts.

I	II	III	IV	V	VI	VII
Heating Curr. amp.	$I \times 10^{11}$ amp/cm²	T °K	$\log_{10} I/T^2$ +19	$1/T$ $\times 10^7$	$b/2.3T$	$\log_{10} A$
3.1	0.0406	1367	0.337	7315	23.02	4.357
3.3	0.152	1406	0.887	7112	22.38	4.267
3.5	0.607	1444	1.467	6925	21.79	4.257
3.7	2.07	1480	1.977	6757	21.26	4.237
3.9	6.91	1515	2.478	6601	20.77	4.248
4.1	21.25	1549	2.946	6456	20.32	4.266
4.3	61.20	1583	3.387	6317	19.88	4.267
4.5	164.0	1618	3.795	6180	19.45	4.245
4.7	410.3	1651	4.178	6061	19.065	4.243
4.9	1000.	1683	4.546	5942	18.70	4.246
5.1	2322.	1715	4.896	5831	18.35	4.246
5.3	4470.	1745	5.229	5731	18.035	4.254
					Average	4.252

The points when plotted as in Fig. 3 fit the straight line relation very accurately, no point being further off than could be accounted for by an error in the temperature of 0.5°. The value of b obtained from the slope is 72,450°K. Using this value for b the average value of log A as shown in the last column is 4.252, corresponding to $A = 17{,}850$ amp/cm² deg². Aside from the first reading for which the thermionic current was too small to be measured accurately, the maximum deviation from the mean value of log A is 0.37 percent corresponding to a 3.5 percent deviation in A itself which must

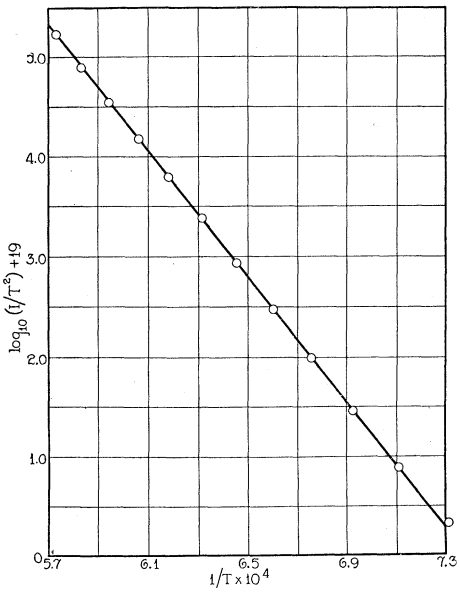

Fig. 3. Thermionic curve for clean platinum.

be considered a very satisfactory agreement. When corrected for the Schottky effect, the values obtained are

$b = 72,820°K$

$\phi = bk/e = 6.27$ volts.

$A = 17,000$ amp/cm^2 deg^2, approx.

The above values were obtained under very good conditions and are good averages of the results obtained in many other runs on various specimens of platinum. They are believed to be close to the true values for the clean metal. It will be noted that the value for ϕ is slightly less than that given by the previous less precise measurements[12] ($6.35 \pm .1$ volts) though it is within the limits of error of those measurements. Due to the greater precision the present value is probably more reliable. It is in even better agreement with the value 6.30 volts previously obtained for the photoelectric work function. Assuming the correctness of the Worthing temperature scale the above value for ϕ should not be in error by more than 0.5 percent. Because of this uncertainty however the error may be 1 percent or slightly more, so that the best value of the work function given by the present data is $\phi = 6.27 \pm 0.07$ volts.

It is impossible to be certain of the value of A to better than possibly 25 percent. However it is clear that the value obtained is at least 250 times greater than the theoretical value of 60.2 observed for other metals. If the value $A = 60.2$ be assumed and b calculated from the data we find,

for $T = 1406°K$, $b = 64,500°K$; $T = 1651°$, $b = 63,300°$; $T = 1745°$, $b = 62,500°$,

which do not agree with each other and which differ from the value given by the slope of the curve by from 11 to 14 percent. The value 60.2 thus cannot possibly be reconciled with the present measurements. Bridgman[13] has shown that the observed value of A can be accounted for without doing violence to the otherwise satisfactory theories of thermionic emission by the very simple assumption that the surface work function (photoelectric) varies slightly with temperature. This theory and its relation to the present results and to the variations in A *during* outgassing have been discussed in another paper.[7]

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

California Institute of Technology,
August 20, 1928.

[12] There is an unfortunate error in labelling the ordinates of Fig. 3 of the second paper of reference 5. These numbers should read 0.8, 1.6 and 2.4 instead of .4, .8, and 1.0 resp.

[13] Bridgman, Phys. Rev., **31**, 862 (1928).