A COMPARISON OF THE THERMIONIC AND PHOTO-ELECTRIC WORK FUNCTION FOR PLATINUM.

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SYNOPSIS.

Variation of Photo-electric Effect with Temperature, to 420°.—(1) *Pt filaments coated with oxides of Ba and Sr* were mounted in an evacuated tube with a quartz window and could be heated electrically to any desired temperature. The *photo-electric current* received by a copper oxide coated Faraday cylinder when a strip was illuminated with light from a quartz arc was measured with a sensitive electrometer, and was found to increase rapidly with the temperature reaching a value, on first heating to 420°, about 68 times as great as at 20°. The *long wave-length limit* was found to shift with increasing temperature from 2860 to about 3800 Å, the corresponding *work function* changing from 4.31 to 3.24 volts. On cooling, however, the sensitiveness and wave-length limit did not return to their original values, except very gradually, showing marked *time-lag effects*, due probably to changes in the oxide surface. (2) *Pt strips*, uncoated, were tested in the same manner. After preliminary treatment by repeated heating to 900°, the *current* was found to be independent of the temperature to 500°, except for a slight decrease due to the magnetic effect of the heating current, and the *long wave-length limit* remained constant within one per cent. at 2570 Å. Hence the *work function* or work necessary to detach an electron photoelectrically from Pt comes out 4.80 volts, which is close to the values found for the corresponding thermionic work function.

Relative Energy of Spectrum Lines of Hg, 2301 to 2804 Å from an arc in quartz, after dispersion by a quartz spectrograph, was determined with a Coblentz thermopile.

Variation in Resistance of Pt with Temperature to 600° was measured (Table I.).

I. INTRODUCTION.

ACCORDING to Richardson,[1] the equation governing the emission of electrons from incandescent solids in a vacuum is

$$i = AT^{\frac{1}{2}}e^{-b/T},$$

where i is the saturation current at a temperature T, from the glowing metal to an auxiliary electrode, A is a constant of the glowing substance which may be associated with the number of free electrons per cubic centimeter of the body in question, T is the absolute temperature, and b is a characteristic constant of the body which is identified with the work necessary to bring one electron out of the body. This work may be expressed in volts through the relation $\varphi e = bK$, where e is the electronic charge, K is the gas constant for one molecule, and φ is the work expressed in equivalent volts. Practically all investigations on thermionic emission

[1] Richardson, Phil. Trans. Roy. Soc., A, 201, 497, 1903.

have been based on this expression, the validity of which may be considered as well established.

The relation governing the emission of electrons from metals in a vacuum under the influence of light was stated by Einstein[1] in 1905 in the form

$$\tfrac{1}{2}mv^2 = Ve = h\nu - p,$$

where ν is the frequency of the exciting light, h is the Planck constant, $h\nu$ is the energy absorbed by the electron from the radiation, p is the work necessary to get an electron out of the interior of the metal, and v is the maximum velocity with which the electron leaves the surface, which can, of course, be determined by the retarding potential V necessary to just prevent such an escape. Though the earlier experiments did not conclusively prove the existence of the necessary relations which follow if Einstein's equation is correct,[2] the more recent experiments[3] all bear out the validity of this equation.

THE WORK FUNCTIONS IN THE THERMIONIC AND IN THE PHOTOELECTRIC EFFECTS.

A. *Thermionic Effect.*—Several methods have been developed to measure the work function in the thermionic effect as represented by the constant b in Richardson's equation. The original method was to take the logarithms of the quantities involved in the equation, *i.e.*,

$$\log i - \tfrac{1}{2}\log T = \log A - \frac{b}{T},$$

and then to plot $(\log i - \frac{1}{2}\log T)$ against $1/T$. Then if Richardson's equation is correct, we should get a straight line relation whose slope would give the value of b. In all of the work by this method an accurately linear relation has been found.

Another method which has recently been used is to measure the cooling effect due to the evaporation of electrons from the surface of the metal. The loss of energy under consideration is analogous to the heat lost during the evaporation of liquids, and it may, in fact, be regarded as the latent heat of evaporation of electricity from the substance in question. The theoretical relations involved have been worked out by Richardson,[4] and some very accurate and consistent results by this method have been

[1] Einstein, Ann. d. Physik, 17, 132, 1905; 20, 199, 1905.

[2] Millikan, PHYS. REV., 7, 355, 1916.

[3] Millikan, PHYS. REV., 7, 18, 1916, and PHYS. REV., 7, 355, 1916. Hennings and Kadesh, PHYS. REV., 8, 209, 1916, and PHYS. REV., 8, 221, 1916. Sabine, PHYS. REV., 9, 210, 1917.

[4] Richardson, Phil. Trans. A., 201, 497, 1903.

obtained by Lester[1] for the case of tungsten, and by Wilson[2] for oxide coated filaments.

The agreement between the two methods is very good as may be seen from the results for tungsten. Using the first method, Langmuir[3] and Smith[4] get for the value expressed in equivalent volts of the work necessary to extract an electron from tungsten 4.25 and 4.46, respectively, while Lester,[5] using the second method gets 4.478 volts. In these experiments, the emission is thought to be a pure electron emission, uninfluenced by gases or surface films. If we are to associate this work with that necessary to get an electron out of the metal, it is necessary that all secondary effects due to occluded gases, surface films, etc., be eliminated. It was believed that this had been accomplished in the experiments cited above, so that these values represent the work function characteristic of tungsten.

B. Photoelectric Effect.—The energy relations in the photoelectric effect are given by Einstein's equation

$$\tfrac{1}{2}mv^2 = Ve = h\nu - p.$$

According to this equation, the maximum velocity of the emitted electrons increases with an increase in the frequency of the incident light, and decreases as we go to longer wave-lengths of the incident light. This is borne out in all of the experimental work on the subject. Further, there will exist for each photoactive material a critical frequency, or wave-length, beyond which the target is no further photoactive. At this critical stage, the equation reduces to

$$h\nu_0 = p,$$

where ν_0 is the lowest frequency to which the target is just photoactive, or the longest wave-length λ_0; and p, as before, represents the work necessary to just get an electron out of the target. Hence, by determining this threshold value of the frequency, or longest wave-length, we should be able to calculate the work, p, as defined above.

In order, however, to be able to interpret this work function as a characteristic constant of the metal itself, it is obviously necessary to eliminate all secondary effects due to surface films or other contaminations.

[1] Lester, Phil. Mag., 31, 197, 1916.
[2] W. Wilson, Proc. Nat. Ac. Sci., 3, 426, 1917.
[3] Langmuir, Phys. Zeits., 15, 525, 1914.
[4] Smith, Phil. Mag., 29, 811, 1915.
[5] Lester, Phil. Mag., 31, 197, 1916.

II. OBJECT OF EXPERIMENT, AND PREVIOUS COMPARISONS BETWEEN p AND b.

The purpose of the experiment was:

1. To study the variation of the photoelectric current from oxide-coated and pure platinum filaments with a change in the temperature of the filaments.

2. To see if a constant long wave-length limit for a substance can be determined which is characteristic of the substance; in particular to test its constancy with respect to changes in temperature.

3. To compare the work necessary to get an electron out of the substance photoelectrically with that required to get it out of the same substance thermionically.

At first it was thought possible to use the oxide-coated filaments used in audion bulbs of the Western Electric Co. as the source, for Wilson[1] had shown that there could be associated with them a definite b. However, in the determination of the long wave-length limit of this material, it was found that this limit was not constant, but changed considerably with temperature. Consequently pure platinum was chosen for this comparison work, since previous experiments[2] had shown that a definite b could be associated with it, as well as a definite long wave-length limit, and hence a definite p. The choice seems to have been a proper one, for a definite long wave-length limit for this specimen has been found which remains constant through a wide range in temperature.

COMPARISONS BETWEEN b AND p.

Considerable work has been done to find the work necessary to get an electron out of platinum by thermionic means. Richardson, in reviewing these researches, discusses[3] these various determinations critically, and concludes that the most probable value of b, expressed in equivalent volts, is about 5.00 volts for platinum. Hughes[4] taking the photoelectric data on platinum from the Richardson and Compton[5] paper compares the value of p in this case with that of the then accepted value of b in thermionics for platinum, both expressed in equivalent volts. But in this comparison, he used for the value of b in Richardson's equation 5.34 volts, while the most probable value for platinum according to Richardson is very closely 5.00 volts. Moreover, he used for the long

[1] W. Wilson, Proc. Nat. Ac. Sci., 3, 426, 1917.

[2] For a summary of these expts. see Richardson, "Emission of Electricity from Hot Bodies," p. 69, etc.

[3] Richardson, "Emission of Electricity," p. 69, etc.

[4] Hughes, "Photo Electricity," p. 44.

[5] Richardson and Compton, Phil. Mag., 24, 575, 1912.

wave-length limit for platinum $\lambda_0 = 2910$Å, from Richardson and Compton's paper, while the experiments described in this paper yield a value of λ_0 about 300Å shorter than this. If these newer values are used in the comparison, the photoelectric work function comes out very close to the thermionic, namely 4.80 volts at ordinary temperatures against 5.00 volts at the mean temperature of the thermionic emittor which may be taken as about 1100° C.

Hagenow[1] made a similar calculation for the case of tungsten. He concluded from his experiments that the long wave-length limit for tungsten must lie between the values 2100 and 2300Å, which are equivalent to 5.87 and 5.37 volts respectively. These values are much higher than that given by Lester's[2] work, namely 4.478 equivalent volts.

III. Apparatus and Procedure.

A. *The Oxide-Coated Filaments.*—The filaments were made by the Western Electric Company and consisted of platinum strips 1 mm. wide coated with the oxides of Ba and Sr in equal amounts. Four of these were welded in parallel to stout platinum leads in such a manner that the oxide of the center portions of the strips, upon which the ultraviolet light fell, were unimpaired. This target was mounted in a glass tube about 3 cm. in diameter, closed by a thin quartz plate cemented to the tube by DeKhotinsky cement. A Faraday cylinder of oxidized copper served to catch the emitted electrons, and the quantity given off was measured by a Dolezalek quadrant electrometer, which could be brought to a sensitiveness of 5,000 divisions per volt, although this high sensitivity was usually not necessary in the case of these filaments, and a capacity was frequently put in parallel with the electrometer. In the first portion of the work, a Toepler mercury pump was used to obtain the vacuum, and in the latter part a mercury diffusion pump. Liquid air kept mercury vapor out of the experimental chamber. The pressures were as low as 3×10^{-8} mm. of mercury. The temperature of the target was obtained by observing its change in resistance with temperature. In the earlier portion of this work on the oxides, an ordinary quartz spectrometer was used, in the latter work a Hilger monochromatic illuminator. The energy content of the individual lines in the spectrum was greater in the former than with the Hilger instrument, but the relative results were the same. A quartz mercury arc lamp of the Haraeus type served as the source of illumination in all of these experiments, the lamp always being run at a certain constant energy consumption.

[1] Hagenow, PHYS. REV., 13, 416, 1919.

[2] Lester, Phil. Mag., 31, 197, 1916.

B. *The Platinum Emittor.*—A thin strip of platinum foil, 6 × 20 mm. and .0005 inch thick was riveted to stout platinum leads, two fine platinum leads were welded to these leads close to the strip in order to measure the potential drop across it, and the whole was then mounted in the center of a glass tube of about 3 cm. in diameter. A Faraday cylinder enclosed the strip except for small openings for the heating current and potential leads and the opening for the incident light. Figs. 1 and 2 will give an idea of the arrangement within the tube, and of the experimental arrangements.

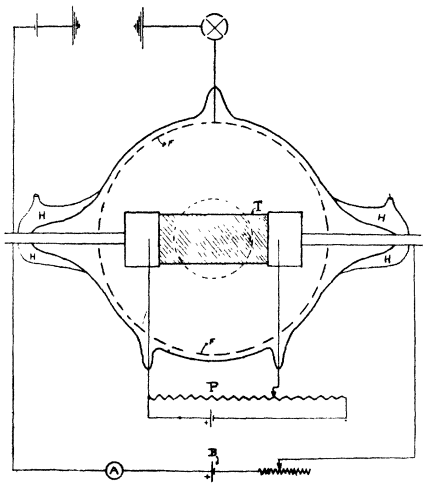

Fig. 1.

It was found that at higher temperatures, the lead-in wires became very hot, and to prevent cracking of the tube, two glass cups *H* were fitted to the tube and lead-in terminals and filled with mercury. This arrangement was found to be very satisfactory. The quartz window in this tube was cemented to the glass by a special material kindly furnished by the Mantle Lamp Company of America. This cement can be heated to 200° C. without danger of getting soft or impairing the vacuum.

The temperatures of the platinum strip were measured by its change in resistance with temperature. A temperature-resistance calibration curve was first taken, in which the strip was placed in an electric furnace and its resistance determined directly up to 650° C. In this calibration, the lower temperatures were measured by a standardized high temperature mercury in glass thermometer and the higher by a platinum resis-

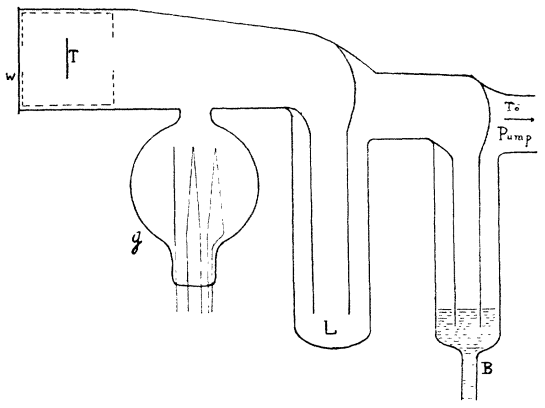

Fig. 2.

tance thermometer. According to Chappuis and Harker[1] the resistance of platinum changes with the temperature in the range from 0–500° C. according to the formula

$$R_t = R_0(1 + \alpha t + \beta t^2)$$

where R_t is the resistance at the temperature t, R_0 is the resistance at 0° C., and

$$\begin{aligned} \alpha &= \quad .003922, \\ \beta &= -.0_6585. \\ &= -.000000585 \end{aligned}$$

Table I. shows the resistance of the strip calculated from this formula and compared with the observed resistance taken from the resistance-temperature curve. The resistance at 0° C. was 1.010×10^{-2} ohms.

TABLE I.

	Observed.	Calculated.
Resistance at 100° C.	1.42×10^{-2}	1.41×10^{-2}
200° C.	1.82	1.80
200° C.	2.21	2.20
400° C.	2.58	2.57
500° C.	2.95	2.99
600° C.	3.29	3.38

The potential drop across the strip being small, a potentiometer arrangement P was used to measure it. The current necessary to heat the filament was furnished by a set of storage batteries B.

The apparatus (Fig. 2) was exhausted by a mercury diffusion pump working against a fore-vacuum of about .001 mm. of mercury produced by a Gaede rotary mercury pump. A barometer tube, B, served as a valve to shut off the left-hand side of the apparatus, if desirable. L is the liquid air trap. The pressures were measured by means of a Buckley[2] ionization gauge, G. The electron current used with this gauge was measured with a Paul single pivot micro-ammeter, the plate current by means of a sensitive galvanometer. The pressures used varied from 1×10^{-5} to 1×10^{-6} mm. of mercury. T is the platinum strip, and W the quartz window.

The source of light for the illumination of the strip in all of these determinations was the quartz mercury arc lamp mentioned before. It was enclosed in a box, so that it could be run at a high temperature. Souder[3] found that under these conditions the energy output of this lamp remained very constant for many hours. The energy distribution

[1] Land. and Bornst, Tables, 1912, p. 1083.

[2] Buckley, Proc. Nat. Ac. Sci., 2, 683, 1916.

[3] Souder, PHYS. REV., 8, 683, 1916.

in the various prominent lines of the mercury spectrum emitted by the lamp was determined by means of a Coblentz thermopile and a shielded galvanometer. The values obtained in this work of the relative energies of the mercury lines used most frequently are given in Table II.

TABLE II.

Wave-Length.	Deflection ∝ Energy.
2301A°	1.13
2378	2.31
2400	3.02
2483	6.26
2537	16.38
2652	13.68
2700	5.46
2804	11.48

The method of obtaining λ_0 in these experiments was the direct method described by Millikan.[1] The relative energy content of the various lines in the spectrum used being known, their relative photoaction is measured and then the photocurrent per unit intensity of the line is plotted against the wave-lengths. A smooth curve is drawn through the points and continued so as to cut the wave-length axis. This gives the longest wave-length to which the metal is just photosensitive. The results obtained by this method after the metal had been sufficiently denuded of gases were remarkably consistent as is shown below.

IV. RESULTS.

A. *The Oxide-Coated Filaments.*

Variation of Photoelectric Current with Temperature.—In 1906 Millikan and Winchester[2] and Lienhop[3] independently established the lack of dependence upon temperature both of the amount and of the maximum value of the velocity of emission of photoelectrons. The former used eleven metals in the same tube, and their temperature range was from 15° to 125° C. The latter used carbon and platinum, and his temperature range was from room temperature to − 190° C. Ladenburg[4] found that the velocities of photoelectrons from AU, Pt and Ir were independent of the temperatures up to glowing. All of these authors used the whole radiation from their respective sources, that is, they did not attempt to determine the long wave-length limit of their substances

[1] Millikan, PHYS. REV., 7, 355, 1916.

[2] Millikan, PHYS. REV., 24, 6, 1907, and Phil. Mag., 14, 188, 1907.

[3] Lienhop, Ann. d. Phys., 21, 284, 1906.

[4] Ladenburg, V. d. D. P. G., 9, 165, 1907.

at these various temperatures. All of the subsequent experimental work has supported the results obtained by the above-mentioned authors as regards the independence of the maximum velocity of emission of photoelectrons and temperature. Varley and Unwin[1] found a constancy of photoelectric current from platinum at a pressure of .0035 mm. of mercury, but only after a certain heating current had been applied to the platinum foil so as to raise its temperature to at least 50° C. Beyond this point the photoelectric current remained practically constant up to a temperature of 350° C.

The behavior of these oxide strips, however, was quite different from the above, the photoelectric current greatly increasing with a rise in temperature, the rate of increase always being far greater the higher the temperature. A typical set of readings follow in Table III., all readings being for line 2537Å, the time unit being 30 seconds and the incident light remaining constant:

TABLE III.

Oxide Coated Filaments. Variation of Photoelectric Current with Temperature.

Temperature.	Deflections ∝ Photoelectric Current.
20° C.	2.0 cm.
47	2.0
75	2.0
120	2.6
160	4.2
200	5.5
240	14.2
270	16.6
310	20.6
350	39.6
420	135.0
Then, ten minutes after the heating current in the last reading above was thrown off, and the target had returned to	
20° C.	141.0 cm.

It may be remarked that these deflections did not change abruptly as the higher heating current was thrown on, but that there was a gradual change toward a higher value as the heating at any particular temperature was continued, the rate of increase in all cases being most rapid when the heating current was first applied. After heating for some time at a constant temperature, the deflections become relatively constant. In the above particular set of readings, after the apparatus had stood for seven days at room temperature, the deflection had decreased to 40.0 cm., *i.e.*, they had not returned to their original value. How quickly and how nearly the original values of the photoelectric current were reached again depended altogether upon the temperature to which the target

[1] Varley and Unwin, Proc. Roy. Soc. Edinburgh, 27, 117, 1907.

had been heated during the run, the return being quicker and more complete the lower the temperature to which the target had been heated. Even after four months the original value of the photoelectric current had not been reached although the deflections had decreased to 4.7 cm. Another peculiar behavior was always noted in that, immediately after the heating current was switched off, and the target had returned to room temperature, the photoelectric current always increased over that of its maximum value at the maximum heating current, and it was not until hours after, that it began to decrease. This behavior of the oxide strips was absolutely general, whether for high or lower vacuum condition.

Variation of the Long Wave-Length Limit with Temperature.—Along with this 68-fold increase in the amount of the photoelectric current, the long wave-length limit of these strips also changed as the temperature was raised. The long wave-length limit of the filaments in the beginning of the experiments was about 2860Å. As the heating progressed, it was observed that this limit was shifting toward the longer wave-lengths. At the highest temperature used in the above data, the target was certainly photoactive at $\lambda = 3650$Å, but not when illuminated with the visible violet line 4047Å. Without appreciable error, the long wave-length limit at the highest temperature above may be taken as 3800Å. As time went on, the long wave-length limit would slowly shift again towards the shorter wave-lengths.

Using the relation $p = h\nu_0$, the work necessary to get an electron out of this target by photoelectric means amounts to 4.31 volts at 20° C., and to 3.24 volts at 420° C. This latter value is about of the same order as found by Wilson[1] for the thermionic work function for these oxide strips.

The cause for this increase in the photoelectric current, and the decrease in the work function with an increase in temperature need not be ascribed to a change in the work function of the unchanged surface with temperature, but rather to the fact that the surface of the oxides was changed and hence changed the photoactive properties of the target. That a change in such targets actually does occur at higher temperatures was shown by Fredenhagen,[2] namely that the oxides gradually disappear and the underlying platinum shows corrosion. Assuming, then, a surface change with heating of the oxide coated filaments, it can at least be said that in this change the target is put in a condition where the work to get an electron out of it is much less at higher than at lower temperatures.

[1] W. Wilson, Proc. Nat. Ac. Sci., 3, 426, 1917.

[2] Fredenhagen, Ber. d. Saechs. Ges. d. Wiss. Math. Phys. Kl., 65, 55, 1913.

B. *The Platinum Emittor.*

The procedure was similar to that used with the oxide emittor. The platinum was very weakly photosensitive at first, the deflection for the strong 2537 line only amounting to 0.6 cm. in 30 seconds, and an increase in temperature gave an increase in photosensitiveness similar to that observed with the oxide strips. After the platinum had been repeatedly heated to temperatures of 900° C. and more, however, the behavior was different. The photoelectric current no longer increased with a rise in temperature, but rather appeared to decrease slightly. This decrease was presumably due to the magnetic effect of the heating current upon the escaping electrons. The absolute values of the photoelectric current varied somewhat from day to day, but the value of the long wave-length

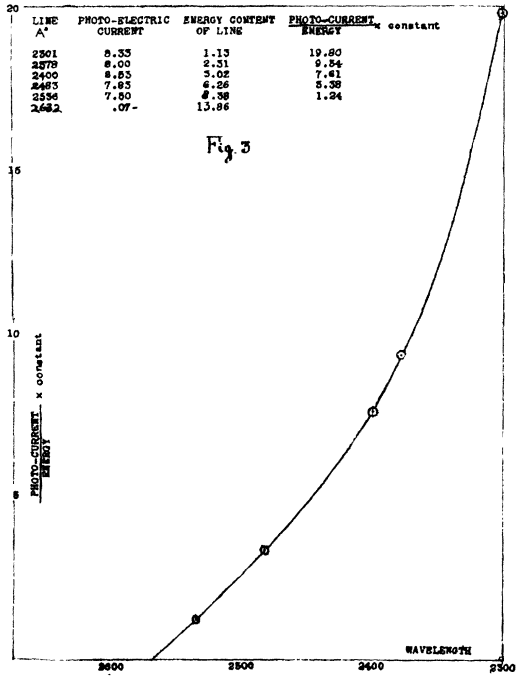

Fig. 3.

limit of the platinum remained constant. This variation of the photoelectric current does not affect in any way the determination of the long wave-length limit, since the photoelectric currents due to the respective lines were affected alike.

The Long Wave-Length Limit Determinations.—The method of determining the long wave-length limit of the platinum strip was the direct

method described by Millikan[1] in his work on sodium and lithium. The relative energy content of the lines in the mercury spectrum of the mercury arc having been determined, the photoelectric current per unit intensity was plotted against the wave-length and the intercept of this curve with the abscissa gave the longest wave-length to which the platinum was photosensitive. At first the platinum showed a behavior somewhat similar to that of the oxide strips, though less marked. Thus the long wave-length limit shifted toward the longer waves as the temperature was raised, and then shifted slowly back toward the shorter waves when left standing for a time at room temperature. But after glowing out for several hours with a 9.0 amperes heating current, which raised the platinum foil to bright red heat, the behavior of this platinum was constant as regards its long wave-length limit. In the process of this outglowing the pressure rose only very slightly, so that if gas was emitted from the strip, the speed with which it was emitted was certainly less than the speed of evacuation. Taking then the values of the photoelectric currents at various temperatures and plotting them as shown in the sample plot of Fig. 3 we get the set of long wave-length determinations as shown in Table IV.

TABLE IV.

Temperature.	Long Wave-Length Limit = λ_0.
20° C.	2571A°
100	2560
370	2568
490	2564

It may be added that even after the original tube had to be discarded and another tube containing the same platinum strip had been constructed, the result as regards the long wave-length limit was not altered in the least after the platinum had again been brought to a steady state. Thus the threshold wave-length at which the platinum begins to be photoactive may be taken as 2570Å at room temperature, and this value varies but little if at all with a change in temperature up to 500° C. It is believed that this is a constant which is an intrinsic property of platinum. This value is about 300Å shorter than the value of the long wave-length limit for platinum found by Richardson and Compton[2] who get 2880A for this constant.

If we take then the long wave-length limit for platinum as 2570Å, we can compute the work necessary to emit an electron by photoelectric means, *i.e.*

[1] Millikan, PHYS. REV., 7, 355, 1916.

[2] Richardson and Compton, Phil. Mag., 24, 575, 1912.

$$p = h\nu_0 = \frac{6.547 \times 10^{-27} \times 3 \times 10^{10} \times 3 \times 10^{2}}{4.774 \times 10^{-10} \times 2.570 \times 10^{-5}} = 4.80 \text{ volts.}$$

In the thermionic effect, Richardson inclines to the values of b, expressed in equivalent volts, as determined by Deininger[1] and Horton[2] who get 5.02 and 5.1 volts, respectively, for the work function in the thermionic effect of platinum.

The Variation of the Work Functions with Temperature.—The work function in the thermionic effect has been found to change very little, if any at all, with temperature in the ranges of temperatures usually employed. The same may be said for the photoelectric work function, as may be seen from Table IV., at least it does not change appreciably in the range from room temperature to 500° C. Above this temperature it becomes more difficult to determine the long wave-length limit because the thermionic effect becomes appreciable, so that the photoelectric current must be determined by difference measurements from the superposed effects of the two phenomena. This was done with temperatures up to about 700° C., and an increase in the long wave-length limit was observed, amounting to as much as 50A at these higher temperatures. Further tests will be necessary upon this point, but in view of the ease and definiteness with which the intercepts on the wave-length axis can be determined, it seems probable that the method will yield a simpler and more sensitive test of the temperature variation of the work function than can be found in measurements upon the thermionic effect.

I wish to thank Messrs. Julius and Fred Pearson, mechanicians at the Ryerson Physical Laboratory, for their work and suggestions in connection with the construction of the tubes used in these experiments.

Finally, I wish to express to Professor Millikan my appreciation for suggesting the problem and for his continued interest and assistance in the course of these experiments.

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[1] Deininger, Ann. d. Phys., 25, 285, 1908.
[2] Horton, Phil. Trans. A, 207, 149, 1907.