THE PHOTOELECTRIC PROPERTIES OF THOROUGHLY OUTGASSED PLATINUM[1]

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Abstract

Effect of heat treatment on the photo-currents from Pt.—The total photoelectric emission from a strip of Pt foil excited by the full radiation from a quartz mercury arc was studied while the strip was put through an extended heat treatment in pressures as low as 10^{-8} mm Hg as read on an ionization gauge. Prolonged heating at 1200°–1400°C caused the photo-current to decrease to a final value which could not be further reduced by additional heating for as long as 300 hours at temperatures up to the melting point. The photo-current was found to increase spontaneously from the low values observed immediately after a heating interval to much higher values if the strip was allowed to remain at room temperature for a short time. After thorough outgassing of the strip and the tube however this "recovery" effect finally disappeared.

Effect of heat treatment on the long wave-length limit of Pt.—The long wave-length limit was determined by using filters of dilute acetic acid in a fluorite cell to cut out the shorter Hg lines. The threshold was found to shift during outgassing from above 2500A to a final steady value of 1958 ± 15A. This is at variance with Suhrmann's value of 2675A but is shown to be in agreement with the work of Tucker and Woodruff. Pressure readings taken with an ionization gauge of high sensitivity confirm the conclusions (a) that decreasing photo-currents are caused by the evolution of absorbed gases, (b) that increasing photo-currents (recovery effect) are due to the adsorption of gas by the cool Pt surface, and (c) that the final low values of the photo-emission are characteristic of the gas-free Pt. Heating an outgassed strip in air at 0.015 mm pressure caused the photo-currents to disappear; heating in hydrogen at the same pressure caused them to increase. They were brought back to values characteristic of the completely outgassed state in each case by heating for 30 sec. at a pressure of 10^{-6} mm.

Influence of temperature on the photo-emission from Pt.—The photoelectric effect of Pt is found to be independent of the temperature only in the region below 500°C. At higher temperatures up to 1200°C the photo-currents increase considerably with temperature and the threshold shifts slightly to the red. Several explanations of the effect were tested and are discussed, the conclusion being that it is a genuine temperature effect characteristic of the metal itself and due to the increase in the thermal energies of the "free" electrons which may become appreciable at the higher temperatures.

Introduction

IN SPITE of the large amount of recent research on the subject, the status of the problem of the photoelectric behavior of metals which have been thoroughly cleaned of occluded gases is still a rather un-

[1] A preliminary report of this work appeared in Proc. Nat. Acad. Sci. **12**, 162 (1926).

certain one. Strange to say, however, the principal points of disagreement between various observers lie not so much in the experimental facts observed as in the conclusions drawn from them and in the explanations offered. In the case of platinum, for example, while there is general agreement as to the type of behavior observed when the photo-current excited by the radiation from a quartz mercury arc is studied as a function of the time for which the specimen has been outgassed by heating, there are still three questions at least upon which the experimenters in this field are divided, namely: (1) the old problem of whether the observed decrease in the photo-current with outgassing continues indefinitely, or whether it is possible to reach a limiting state characteristic of the cleaned metal itself; (2) the question as to which, if any, of the many observed values of the photoelectric threshold may be accepted as the true value characteristic of the platinum; (3) the problem of formulating a theory to explain the effects of gases and to account for the observed results. The experimental work to be described in the present paper was undertaken for the purpose of obtaining further evidence on all three of these questions. Reviews of previous work in this field have been given by other writers[2] and only a brief statement of the present status of each problem will be given here.

In regard to the first, Wiedmann and Hallwachs[2] and their students have been led to the view that the photoelectric effect is not an intrinsic property of the metal at all but that, as outgassing progressed, the photo-currents excited by the light ordinarily used would disappear, and the long wave-length limit would shift steadily further into the ultra-violet, reaching finally the region near 1200A where ionization of the gas atoms themselves begins. Other observers[3,4,5] are inclined to the view that the platinum itself is the seat of the photo-currents and that the absorbed gases merely assist (or hinder) their escape; that it should be possible to reach a state where the photo-currents from the Pt itself are obtained and where the threshold, while it may be far in the ultra-violet, still has a value characteristic of the cleaned metal, unaffected by the presence of gases. Actually to reach such a state has proved to be a difficult task.

The second problem, that of the characteristic long wave-limit of Pt, is thus seen to be intimately connected with the first. Observed values of the threshold have been pushed steadily to shorter wave-lengths as more complete outgassing has been attained, and Tucker[6] and

[2] See Wiedmann, Jahrb. d. Radioakt. u. Elekt. **19**, 112 (1922). See also refs. 5, 6, 9.
[3] Welo, Phys. Rev. **12**, 251 (1918); Phil. Mag. **45**, 593 (1923).
[4] Piersol, Phys. Rev. **8**, 238 (1916).
[5] Woodruff, Phys. Rev. **26**, 655 (1925).
[6] Tucker, Phys. Rev. **22**, 574 (1923).

Woodruff[5] have reported specimens which were insensitive to the mercury arc radiation for a short time after long heating. Tucker concludes that this indicates a threshold below 1850A though Woodruff believes it may be as high as 2200A because of the observed weakness of the shorter lines in the spectrum. Suhrmann[7] on the other hand reports a limiting value of 2675A after long heating. Obviously before acceptable final values of the threshold can be obtained, a stable limiting state of the specimen must be reached in which the photo-currents remain unchanged during further intense treatment. This condition has not heretofore been realized in the case of Pt, though Kazda[8] seems to have attained an analogous condition in the case of flowing mercury.

The third problem—that of formulating a theory to account for the effects of gases—has also presented difficulties. The theory which has been most widely accepted as explaining the largest number of observed facts is that of Wiedmann and Hallwachs[9] who assumed, (a) that the initial low sensitivity observed for a fresh platinum specimen is due to the presence on the surface of an adsorbed layer of electro-negative gases which tends to prevent the escape of electrons, this surface layer being quickly removed by the heat treatment giving rise to a large initial increase in the photo-current; (b) that in addition there are gases absorbed within the body of the metal itself which in some way aid in the ejection of electrons, and their gradual removal during heating causes the photo-current to decrease slowly and the threshold to shift into the violet. The implied consequence of this theory was that if all absorbed gases could be removed the photo-currents would disappear.

These assumptions have been confirmed in many respects by the experimental work of Sende and Simon,[10] Suhrmann,[11] and Herrmann,[12] but Welo,[3] Piersol[4] and Woodruff[5] have been led to the conclusion that they do not account for many observed facts. The latter observers regard the Pt as the seat of the photo-electrons and believe that occluded gases retard rather than assist in their emission. An attempt was made in the present work to obtain a more direct test between these viewpoints.

METHOD

Several experimental tubes of slightly different forms were used, a diagram of one of the later ones being shown in Fig. 1. The specimen

[7] Suhrmann, Zeits. f. Physik **33**, 63 (1925).
[8] Kazda, Phys. Rev. **26**, 643 (1925).
[9] Wiedmann and Hallwachs, Verh. d. Deutsch. Phys. Ges. **16**, 107 (1914).
[10] Sende and Simon, Ann. d. Physik **65**, 697 (1921).
[11] Suhrmann, Ann. d. Physik **67**, 43 (1922); Zeits. f. Physik **13**, 17 (1923).
[12] Herrmann, Ann. d. Physik **77**, 503 (1925).

to be tested consisted in a strip of Pt foil, .01 mm thick, 2 mm wide and about 10 cm long, hung in the form of a loop inside the receiving cylinder C of nickel or molybdenum. The strip could be heated by a current from a 20 volt storage battery conducted in through the tungsten leads T to which the strip was spot-welded. Its temperature could be measured by means of an optical pyrometer focussed onto it through the thin window W. The true temperature was determined

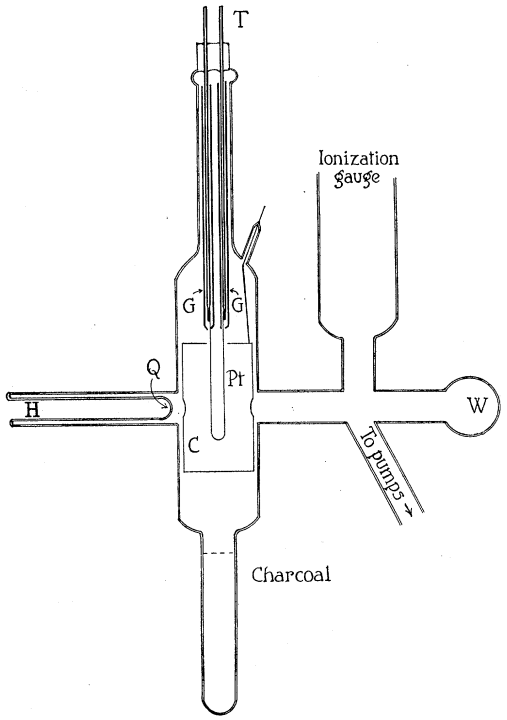

Fig. 1. Photo-electric tube. Q, quartz window; W, pyrometer window; c, collecting cylinder; GG, Pyrex tubes to shield tungsten leads, T.

from the observed black body temperature using data published by Mendenhall.[13] Light from a Cooper-Hewitt Type Y, 110 volt quartz mercury arc, or from a metallic spark, could be focussed by means of a quartz lens through the quartz window Q onto the Pt. The window Q was sealed to the pyrex tube without the use of wax or cement by a graded quartz to pyrex seal. Since nearly all the runs were carried out at pressures below the range of measurement of the McLeod gauge these lower pressures were measured by a sensitive ionization gauge of the type described by Dushman and Found.[14] The apparatus was

[13] Mendenhall, J. Astroph. **33**, 91 (1911).
[14] Dushman and Found, Phys. Rev. **23**, 734 (1924).

connected to the pumps without the use of wax or cement joints to avoid troubles arising from their use. Outgassing at 550°C was possible.

The photo-currents were measured by a Compton electrometer whose sensitivity was 5000 mm per volt. A resistance of 400 megohms shunted across the quadrants permitted the currents to be measured by the "steady deflection" method, the current sensitivity being 5×10^{-13} amp/mm.

In order to prevent scattered light from striking the tungsten supports T, or the upper parts of the strip which were not thoroughly outgassed, these were kept well above the top of the cylinder and were enclosed in small pyrex tubes GG which prevented light of shorter wave-lengths from reaching them and also prevented any electrons leaving them from reaching the cylinder. All of the observed currents then came from the lower parts of the strip which were heated to a uniform temperature.

To furnish to the strip if necessary more energy in the shorter wave-lengths, the region H could be converted into a hydrogen discharge tube by an obvious device. The hydrogen discharge is known to be rich in wave-lengths between 2200A and 1600A.

After an initial cleaning of the Pt, the entire apparatus was baked out at temperatures up to 550°C for periods varying from several hours to several days—or until the pressure with the tube hot had been reduced to 10^{-6} mm Hg or less. In some cases the Pt strip was glowed at a dull red heat during baking. After this treatment the photo-current was quite large, its actual value depending upon the time for which the treatment had been continued in each particular case. The Pt strip was then heated by an electric current for various intervals of time and at various temperatures, photo-current readings being taken intermittently during the process. The heating current through the strip was shut off while the photo-current was being measured. During the heating at higher temperatures the cylinder C could be rotated about a vertical axis by means of an external magnet to bring the holes in the cylinder out of line with the windows Q and W to prevent condensation of platinum on these windows.

The Total Photoelectric Current

Photo-current readings using the mercury arc as a source were taken on 15 different specimens of Pt, cut from foil obtained from three different sources, all of high purity. The strips were subjected to a variety of cleaning treatments before being introduced into the tube, and to many different forms of heat treatment after being sealed in. All, however, exhibited substantially the same form of final behavior of the total photo-current as a function of the time of heating, viz., in every case in which the heating was carried on for a sufficient length

of time the photo-current eventually reached a final limiting value, —not zero—which value could not be further reduced by heating of any kind.

Observations on three typical specimens have already been published[1] and those for a fourth are presented herewith (Fig. 2). This curve may be taken as typical of all the runs which were taken. The maxima in the curve at 22 hours and 50 hours of heating are characteristic of the irregularities which often appeared in the first part of the curves and seemed to be due to incidental pressure variations which were unavoidable during the initial stages of outgassing. Many of the curves

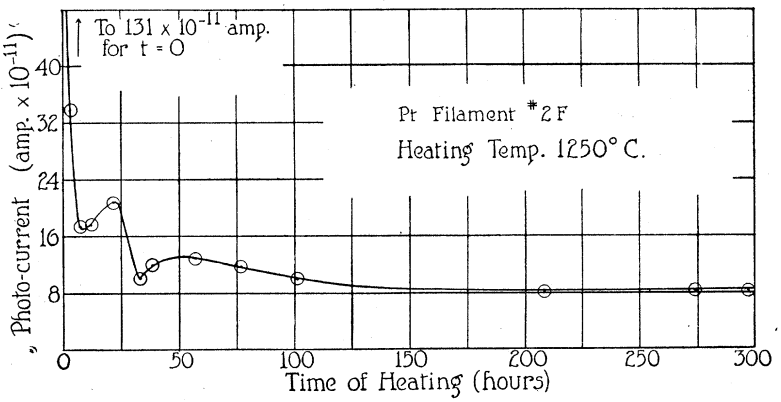

Fig. 2. Variations in the total photo-current during outgassing.

showed no irregularities at all, but in any case they all gradually disappeared as the heat treatment progressed, so that the photo-current approached a limiting value which was truly a stable one.

It should be emphasized that this limiting value is reached only after the heating has been carried on for long periods of time at temperatures higher than 1100°C and at pressures lower than 10^{-6} mm. While the actual number of hours of heating required varied considerably with the temperature and the pressure conditions, in no case was a true final value of the photo-current attained, even at the highest heating temperatures, in less than 10 hours of actual heating time. In most cases at moderate temperatures (1200°–1400°C) from 20 to 50 hours were required, while in some cases, as in Fig. 2, the limiting value was reached only after 150 hours of heating. Furthermore, the value of the photo-current observed in the final outgassed state was the *same* for *all* Pt specimens which were studied under the same set of incident light conditions.

Every effort was made to determine whether this final value of the photo-current could not be reduced by some type of further treatment.

Among the procedures which were tried were the following: (a) heating for still longer intervals of time at the higher temperatures, up to 1500°C; (b) "flashing" intermittently for intervals of a few seconds each at still higher temperatures, close to the fusion point (a procedure suggested as the most effective one by Herrmann[12]); (c) heating for long periods at temperatures at which considerable vaporization of the Pt took place, thus cleaning off the outer surface of the specimen; (d) heating in the immediate presence of a mass of charcoal cooled by liquid air the more rapidly to absorb the evolved gases; (e) heating the strip while the entire tube around it was lowered to liquid air temperatures by means of a copper jacket; (f) further reducing the pressures to as low as 10^{-8} mm by additional baking out and heating of all metal parts at the highest possible temperatures. All these methods were, however, equally ineffective in lowering the final value of the photo-current, though most of them when tried on a fresh specimen did cause it to reach its limiting value more quickly. A thoroughly cleaned specimen is thus still sensitive to the arc radiation.

A phenomenon reported by Woodruff and by Tucker and referred to as the "recovery" of the photo-emission was also studied in this connection. When the Pt strip is allowed to stand at room temperature for a short time immediately after a heating interval, the photo-current increases spontaneously up to a value which depends upon the previous heat treatment and the pressure and which may be only a few percent less than the maximum value observed during the initial stages of outgassing. It was found by the author, however, that this recovery becomes less rapid and the final value reached becomes steadily smaller as the outgassing progresses and the pressures in the tube become smaller. If the outgassing is carried on long enough that the pressures are reduced to below 10^{-7} mm the effect finally disappears entirely and the photo-currents observed immediately after heating remain constant for many hours. This phenomenon will be more fully discussed later in connection with the pressure effects which were found to accompany it. (See Fig. 3.)

The Long Wave-Length Limit

The variations of the long wave-length limit of Pt described in the previous paper[1] have been checked on other specimens, using as before light filters to cut out successively the shorter lines in the mercury spectrum,—a method used by Williamson.[15] These experiments quite definitely place the photoelectric threshold for Pt cleaned by the process already described in the region between the mercury lines $\lambda 1943$ and $\lambda 1973$.

The filters used in these determinations consisted of weak solutions of acetic acid in distilled water, introduced into an absorption cell with

[15] Williamson, Phys. Rev. **21**, 107 (1923).

fluorite windows which was placed in the path of the incident light. The thickness of the fluid layer in the cell was 3.2 cm. Photographs taken with a Bausch and Lomb quartz spectrograph, using Schumann plates,[16] showed that in the light transmitted by the empty cell the shorter mercury lines including λ1850 were present with considerable strength. Distilled water in the cell served to cut out the 1850 line alone, leaving λ1943 still quite strong. A solution formed by adding three drops of 36 percent acetic acid to 25 cc of water when placed in the cell cut out the 1943 line and all below, leaving 1973 still quite strong. Adding six drops of acetic acid to 25 cc of water gave a solution which cut out λ1973. The longer wave-length lines were cut out using the solutions described by Williamson.[15]

When a fresh strip of Pt was tested after a long initial baking at about 500°C the photo-current could be reduced to zero only after all lines of the mercury spectrum up to and including λ2482 had been cut out by filters. The threshold for such a specimen is thus in the neighborhood of 2500A. After long outgassing, however, and after the photo-current had reached its limiting value, it could be reduced to zero by the filter which cut out the 1943 line and all below it leaving λ1973. It was not reduced to zero by cutting out λ1850 alone leaving λ1943. The threshold has thus been shifted to the region between 1943 and 1973A. Using an aluminum spark as a source the threshold was similarly found to lie between the Al lines λ1930 and 1990. The photo-current was taken to be "zero" in the above observations only when no observable deflection of the electrometer was obtained even after its sensitivity had been increased up to its maximum value by increasing the potential on the needle. In every case a current as great as .05 percent of that produced by the total arc radiation could be easily observed. These results appear at first sight to be in conflict with those of Tucker[6] and Woodruff,[5] but there is a possibility, suggested by Woodruff, that in their work the radiation below about 2200A was too weak to be effective.

If we assume the photoelectric threshold for thoroughly outgassed Pt to be in the neighborhood of 1958A and make use of the quantum relation

$$h\nu_0 = \phi e,$$

we may calculate the work function ϕ for such a surface. The value so obtained is 6.3 volts. The commonly accepted value for the thermionic work function of Pt is 5 volts though this is probably not the value for a thoroughly outgassed surface. Langmuir[17] reports a value

[16] The author is indebted to Mr. H. R. Lillie of this laboratory who made up the numerous Schumann plates required.

[17] Langmuir, Phys. Rev. **2**, 452 (1913).

of 6.6 volts for a surface which had been subjected to special heat treatment, and Woodruff also found high values for his outgassed surfaces.

Relation between Photoelectric Currents and Surface Gas-Content

In order to obtain more exact information on the observed variations in the photoelectric emission as related to the corresponding changes in the gas-content of the specimen and the gas pressures in the tube, a close record was kept of the ionization gauge readings during the runs on several Pt strips. The first point of interest in connection with these readings was to determine how the amount of gas being given off by the specimen during heating varied as the outgassing progressed. The readings for a typical run are given in Table I. In this table are

TABLE I

Progressive changes in pressure and photo-current during heat treatment.

Time of heating	Temp. °C	Pressure $\times 10^{-7}$mm		Ratio	Photo-curr. $\times 10^{-11}$amp.
		Fil. cold	Fil. hot		Fil. cold
10 min.	1250°	5.2	120.0	23.1	84.0
3 hr.	"	4.0	14.0	3.5	26.0
19 "	"	3.2	7.3	2.3	21.0
39 "	"	2.2	4.0	1.82	12.0
107 "	"	0.8	1.2	1.50	8.6
296 "	"	0.25	0.25	1.00	8.5
320 "	1360°	0.10	0.10	1.00	8.5

recorded the steady pressures as read by the ionization gauge while the Pt strip was glowing and while it was at room temperature, at various stages during the heat treatment. The pumps were running continuously during all readings.

These readings were taken on the same specimen whose photoelectric behavior is recorded in Fig. 2. It is seen at once that initially the filament was so saturated with gas that bringing it to a temperature of 1250°C caused a 23-fold increase in the pressure in the tube. After 296 hours of heating, however, during which time the photo-current had reached its limiting value, there was no change in the pressure when the heating current through the strip was turned on, showing that the evolution of gas from the specimen had practically ceased. After the readings recorded in the table were taken the strip was heated irregularly at various temperatures up, finally, to the fusion point, over a period of several days while temperature variation runs were in progress. During this time the pressure and the photo-current remained practically unchanged at the final values given in the table. Evolution of gas from the Pt thus ceases only after extended periods of outgassing—and only after this evolution of gas has ceased are stable

values of the photo-current attained. These observations then confirm the view that occluded gases *assist* rather than hinder the escape of photo-electrons and that their gradual removal causes the photo-currents to decrease.

Further confirmation of this view was found in a more careful study of the "recovery" of the photo-current when the strip was allowed to stand at room temperature for a short time. It was found that after such a period of standing, switching on the heating current through the Pt strip released a large amount of gas from the strip causing an instantaneous increase in the pressure in the tube. In the curves of Fig. 3 the magnitude of this pressure increase is plotted as a function of the time for which the strip had been standing cool. After only 50 hours of outgassing (Curves I and II) if the strip was allowed to stand at room temperature for 10 minutes, turning on the heating cur-

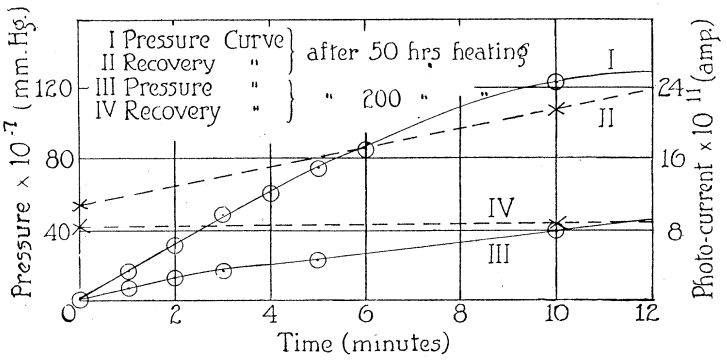

Fig. 3. Recovery of photo-current and accompanying pressure effects.

rent caused a sudden rise in the pressure from 2.0×10^{-7} mm to a peak value of 123×10^{-7} mm. During the same interval the photo-current nearly doubled its initial value. After 200 hours of outgassing (Curves III and IV) the pressure rise due to 10 minutes of standing was only from 1.2 to 40×10^{-7} mm and the rise in photo-current during this interval was only 4 percent. After 300 hours of heating (curves not shown) the rise in pressure as well as the increase in photo-current had practically ceased. The pressure rise caused by heating after a 10 minute interval at room temperature was only from 0.18 to 0.20×10^{-7} mm and after a two hour interval was only to 1.1×10^{-7}. The photo-current during the 10 minute interval now remained constant within the limits of observational error and in the two hour interval increased less than 8 percent.

These results point at once to the conclusion that the recovery of the photo-current is due to the formation on the cool Pt surface of a

gas layer which *increases* the photo-sensitivity of the metal. This layer evaporates at once when the strip is again heated, causing the instantaneous rise in pressure observed. When the Pt strip as well as the rest of the tube have been thoroughly cleaned of occluded gases this surface layer no longer forms and the recovery of the photo-current disappears. The fact that both these effects may be made to reappear by admitting a small amount of air into the tube indicates that the surface layer is formed by deposition on the cool Pt of residual gases in the tube. On the other hand the fact that the formation of the layer ceases only after the strip itself has been thoroughly outgassed might lead to the conclusion that the layer was formed on the surface by diffusion of gases from the interior of the metal. More data are needed to settle this point. In any case the above data on the formation of loosely bound surface layers seem to be in definite disagreement with the view advanced by Woodruff and Welo that the low final values of the photo-current are due to the presence of retarding layers, and in favor of the view that they are characteristic of the outgassed Pt itself. A Pt strip when most completely freed from gases is sensitive only to radiation of wave-length shorter than about 1958A.

If then the *final* low values of the emission are characteristic of the metal itself, the *initial* low values observed before any outgassing is begun must be due to a retarding layer formed on the specimen before it is introduced into the vacuum chamber. It seems probable that this may be a layer of oxide or adsorbed oxygen and nitrogen since it was found that heat ng the outgassed strip for 30 seconds in dry air at a pressure of 0.015 mm actually caused the photo-current to disappear. Heating again in vacuum brought the sensitivity back to the value characteristic of the outgassed metal. On the other hand heating the strip in hydrogen admitted through a palladium tube to a pressure of 0.015 mm caused a large increase in the photo-current, and it was again brought back to normal by short heating in vacuum. The high values of the photo-current which persist even after considerable outgassing are thus probably due to the presence of hydrogen, and possibly water vapor, which are notably hard to remove from the tube and which are readily absorbed by the Pt. Herrmann[12] and Suhrmann[11] have arrived at a similar conclusion, which also is consistent with data obtained by Welo.[18]

Variation of the Photo-Current with Temperature

The temperature variation of the total photoelectric current previously reported[1] has been more carefully studied and its existence more firmly established. At temperatures between 1100°C (at which the thermionic emission is just perceptible) and 1250° (above which

[18] Welo, Phil. Mag. (7) **2**, 463 (1926).

the thermionic emission swamps the photoelectric current) the value of the photo-current was obtained by subtracting the electrometer reading obtained when the light from the arc was cut off from that obtained when the light was focussed on the specimen.

The results show that for thoroughly outgassed Pt the ordinarily assumed independence of the photoelectric effect of the temperature holds quite accurately for temperatues below about 500°C. Increasing the temperature of the specimen above this point however causes the photo-current to rise, slowly at first and then more rapidly, until at 1200° it is practically double its value at room temperature. Three explanations for such an effect may be offered, namely: (1) The variation might be due to the change with rise in temperature of the thickness or density of a surface gas layer; (2) it might be due primarily to the heating current through the strip rather than to the temperature, as suggested by the work of Shenstone[19]; (3) it may be a true temperature effect characteristic of the metal.

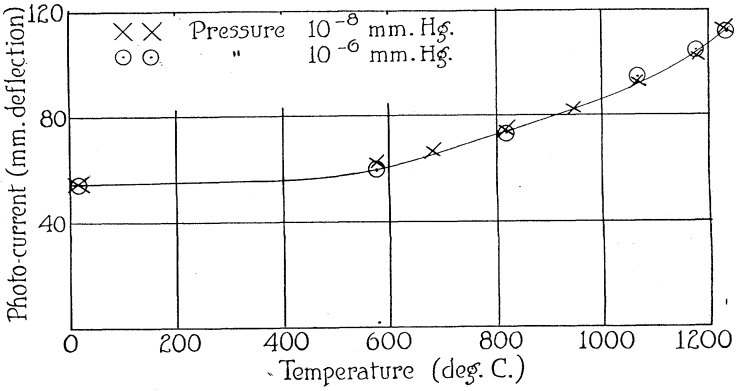

Fig. 4. Temperature variation of the photo-current.

To test the first possibility a large number of runs were taken on several specimens to determine whether the phenomenon exhibited the characteristics which would be expected of a gas effect. The results may be summarized as follows:

(a) The temperature variation described above is characteristic only of the thoroughly outgassed metal. During the earlier stages of outgassing the photo-current showed wide, irregular and non-reproducible changes with temperature, of the type obviously caused by the presence of gas. As the outgassing progressed the behavior gradually became more regular and ultimately settled down to the consistent type of variation shown in Fig. 4.

[19] Shenstone, Phil. Mag. **41**, 916 (1921); **45**, 918 (1923).

(b) When this stage was reached the photo-current—temperature curves taken with temperatures increasing were coincident with those taken with decreasing temperatures,—a result which might not be expected of a phenomenon conditioned by gas-content.

(c) In the thoroughly outgassed state the ionization gauge showed no observable change in pressure in the tube when the temperature of the Pt strip was raised from 20° to 1250°C even when connection with the pumps had been broken by means of a mercury cut-off. The temperature variation thus cannot be due to evolution of gas from the specimen.

(d) The values of the photo-current at the various temperatures were independent of the residual gas pressure in the tube, as long as this was below 10^{-6} mm. In the curve of Fig. 4 the crosses and circles represent points taken with the tube pressure at 10^{-6} and 10^{-8} mm respectively. This result would also not be expected were the photo-currents being affected by the presence of a gas layer, since the characteristics of such a layer should depend upon the surrounding pressure.

It is considered that these results contain sufficient evidence to warrant discarding (1) as a possible explanation of the temperature variation.

That this variation is due primarily to the change in the current through the strip rather than to the temperature seems improbable since the variations of this type reported by Shenstone were very irregular in their nature, showing many time-lag effects when the current was on, and persisting for some time after the current which produced them had been shut off. The variation observed by the author showed none of these effects. Shenstone reported no results for Pt, but it seems evident from the results reported herein that the type of effect which he discovered does not exist for outgassed Pt.

We may then conclude that we are dealing with a true temperature variation of the photoelectric effect. It will be seen from the curve that the type of variation observed is not in disagreement with the results of previous observers who have reported the photoelectric current to be independent of the temperature, since previous observations were carried out in nearly every case at temperatures below about 600°C. It is only at higher temperatures that an appreciable variation is observed.

An increase in the photo-current with rise in temperature might be caused either (a) by an increase in the number of free electrons in the metal made available for ejection by the incident light, (b) by a decrease in the surface work function, or (c) by an increase in the thermal energy of the electrons. In the case of (b) or (c) the increase should be accompanied by a shift in the long-wave limit toward the red while no such shift would occur if the increase were produced by (a) alone.

To determine whether there was such a shift in the threshold, measurements were made of the ratio of the photo-current at 1200°C to that at 20°, *first* using the total radiation of the arc and *second*, when the 1850 line had been cut out by a filter. If these two ratios turned out to be equal this would have been evidence of no shift in the limit. It was found, however, that in the *first* case the ratio was approximately 2 : 1 while in the *second* it was nearly 4 : 1. In other words the change in the photo-current with temperature is greater for the longer wave-lengths (1850 cut out) than for the shorter (1850 included). There has thus been a shift in the threshold toward the red, though it still remained in the region between 1943 and 1973A. Koppius[20] also found evidence for a similar shift in the limit as the temperature was increased from 500° to 700°C. In view of this conclusion (a) must be eliminated as a complete explanation of the temperature variation and we are left to choose between (b) and (c).

Now the work function of a thoroughly cleaned metallic surface is presumably a constant characteristic of the metal itself and is theoretically nearly independent of temperature. Within the (relatively large) limits of error available in thermionic measurements the work function for clean metals is found to be constant over quite wide ranges of temperature. Nearly all the variations in work function (or contact potential) which occur under ordinary conditions can be traced directly to changes in surface contamination,—a factor which it was hoped had been eliminated in these experiments. Moreover any changes in contamination which might be expected to take place with increase in temperature would, in the light of the present results, cause the work function to increase rather than decrease.

We are thus led to conclude that the increase in the photo-current and shift in the threshold toward the red with rise in temperature are due to the increase in the thermal energies of the electrons within the metal. That these thermal energies become appreciable only at the higher temperatures is in line with the postulates of Hall's dual theory of metallic conduction[21] and also with the conclusions to which Millikan and Eyring[22] have been led by their experiments on pulling electrons from metals by intense electric fields. The latter agreement is of interest in its confirmation of the view that the electrons pulled from the metals in these experiments (the "free" or conduction electrons) are the same as those ejected photo-electrically. Moreover if the shift in the threshold is due to the thermal energies of electrons there should be a relation between this shift and the Thomson effect as pointed out

[20] Koppius, Phys. Rev. **18**, 443 (1921).
[21] Hall, Phys. Rev. **28**, 392 (1926).
[22] Millikan and Eyring, Phys. Rev. **27**, 51 (1926).

by Nielsen,[23] and the specific heats of metals at high temperatures, as suggested by the work of Eastman, Williams and Young.[24]

Now in the Einstein photoelectric equation as ordinarily written,

$$Ve = h\nu - h\nu_0$$

Ve represents the maximum energy with which the electrons emerge from the metal, $h\nu$ the energy they receive from the incident light, and $h\nu_0$ is usually assumed to be equal to ϕe, the energy lost by the electron in leaving the surface. Now if the electron through thermal collisions acquires the kinetic energy E_k in addition to the energy received from the incident light, the energy with which it should emerge from the metal is given by

$$Ve = h\nu + E_k - \phi e.$$

On comparison with the previous equation we may now set

$$h\nu_0 = \phi e - E_k,$$

an equation which has also been used by Nielsen.[23] Thus even though the work function ϕ remain constant, ν_0 may alter through a change in E_k in the sense that it will shift slightly to the red at the higher temperatures. As Nielsen has pointed out, the values of E_k will not be the same for all electrons but will be distributed according to Maxwell's law, so that at the higher temperatures the threshold should also show an appreciable lack of sharpness.

Suhrmann[7] has obtained results which he interprets as indicating a shift in the limit toward the red between the absolute zero and room temperature, and also finds an apparent lack of sharpness in the threshold even at room temperature. He attributes both effects to thermal collisions suffered by a few of the electrons even at these lower temperatures. A more detailed study of the variation of the photo-electric threshold with temperature is now being undertaken by the author.

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[23] Nielsen, Phys. Rev. **25**, 30 (1925).
[24] Eastman, Williams and Young, J. Am. Chem. Soc. **46**, 1184 (1924).
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