THE VARIATION IN THE PHOTO-ELECTRIC EMISSION FROM PLATINUM

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Abstract

Photo-electric emission from Pt.—The specimens were ribbons 3 cm by 5 mm by .013 mm thick, mounted in a Pyrex tube with a quartz window. *Effect of heat treatment on sensitivity.* Fresh specimens, cleaned with nitric acid, were insensitive to mercury arc radiation, but became sensitive when heated to moderate temperatures (250°C) by means of an electric current through them, though heating to a much higher temperature in an electric oven was without effect. Prolonged heating (17 hr) at 1300°K with pressure of 10^{-6} mm, reduces the sensitivity to light transmitted by quartz to zero. One specimen so treated remained inactive for 2 months. With pressures below 10^{-7} mm the sensitivity begins to return as soon as heating is stopped, the rate of recovery depending on the wave-length, the pressure and the previous treatment. A specimen insensitive to mercury arc radiation, was sensitive to the radiation from a tungsten filament within the tube, showing that the insensitivity is due to a shift of the threshold to short wave-lengths. *Thermionic measurements* gave an increased value for the work function φ when the threshold λ_0 was shifted to wave-lengths below that transmitted by quartz, in general agreement with the theoretical relation between φ and λ_0. At low pressures, a change of sensitivity in the ratio 1 to 7 was observed without a shift of the threshold wave-length. *Effect of electric field.* After prolonged heating at 10^{-6} mm, small electric potentials, 0.01 to 0.06 volt, are sufficient to prevent the escape of all electrons excited by mercury arc radiation. If the pressure is much lower the electric field shifts the long wave-length limit toward shorter wave-lengths. In both cases photo-activity is not restored when the retarding field is removed but only when an accelerating field is applied. The effect appears to be instantaneous. These results seem to require an adsorbed layer of gas for their explanation. However, the layer formed by heating at high temperatures seems different from that initially present in fresh specimens. This seems to be a retarding ionic layer formed from the residual gas, since at the lowest pressures this seemed to cover only patches of the surface.

Photo-electric measurements with an iron arc, in spite of fluctuations, were made possible by balancing the current against that from a standard cell illuminated by a fraction of the same light by means of a rotating prism and a variable rotating sector.

Introduction

FOR the relation of the energy of an electron emitted photo-electrically to the frequency of the incident light, Einstein has proposed the equation

$$\tfrac{1}{2}mv^2 = Ve = h\nu - w_0 .$$

In this equation w_0 is assumed to be constant for a given substance and equal to $h\nu_0$, ν_0 being the lowest frequency of radiation that is capable of

ejecting an electron. Numerous attempts have been made to check this equation experimentally and to find ν_0 for the various substances. The experiments of Millikan and others,[1] particularly with the alkali metals, have furnished for a number of substances a value of ν_0 which appears to be characteristic of the substance. The experiments with platinum have not been so successful. Among the values first given for the long wave-length limit λ_0 for platinum corresponding to ν_0 is that obtained by Richardson and Compton:[2] viz., 2880A. Later Koppius[3] reduced this value to 2570A. He obtained the lower value simply by baking his apparatus to get rid of gases and by heating his platinum specimens. Two years later, Tucker[4] by still more severe methods of ridding his platinum specimens of gas, was able to reduce λ_0, temporarily, to a value below the shortest wave-length transmitted by quartz.

Wiedmann and Hallwachs and their students[5] working in the Physical Institute, conclude from their experiments with platinum that its photo-activity must be due almost entirely to absorbed gases and that a gas free specimen of platinum would show practically no photo-activity if excited by radiation of wave-length ordinarily used. They conclude that the action of gas upon the discharge of photo-electrons from a metal should be of two kinds; (1) an adsorbed layer of gas on the surface hinders the discharge of photo-electrons, and (2) gas absorbed in the metal assists in the process of discharge of photo-electrons. Indeed, Simon thinks that at least 99.9 percent of the photo-electrons from platinum, obtained by illumination with a quartz mercury lamp, are emitted with the assistance of absorbed gases. Hence if it were not for gases platinum would be photo-electrically inactive. According to this theory, when a metal is heated and the surface film driven off the photo-electric current should increase because the retarding influence of the surface film is removed; while more intensive heating, sufficient to drive out the absorbed gas, should reduce the photo-electric current.

A second consequence of this theory would be that the long wave-length limit should be shifted toward longer wave-lengths by the initial out-gassing because of the removal of the surface layer which retards the slow moving electrons. Further outgassing, which removes the absorbed

[1] R. A. Millikan, Phys. Rev. **7,** 18 (1916); Hennings and Kadesh, Phys. Rev. **8,** 209 and 221 (1916); Sabine, Phys. Rev. **9,** 210 (1917).

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

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

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

[5] Wiedmann and Hallwachs, Deutsch. Phys. Ges. **16,** 107 (1914); Kober and Hallwachs, Phys. Zeits. **16,** 95 (1915); Stumpf, Deutsch. Phys. Ges. **16,** 989 (1914); Sende and Simon, Phys. Zeits. **21,** 562 (1920).

gases, should cause a return of the long wave-length limit to smaller values because the assistance of the forces of the absorbed gases is no longer present.

Suhrmann,[6] working in the laboratory mentioned above, attempted to demonstrate the truth of this theory. He tested the theory in two series of experiments, not only for photo-electric discharge of electrons but also for thermionic discharge of electrons. He used platinum and tantalum in his tests, the results of his investigations being about the same for both metals.

For platinum Suhrmann found that the long wave-length limit shifted from 2600A to 3000A and back again to 2600A as the outgassing process continued. He found that the photo-electric current excited by the wave-length 2650A decreased to a value which was only 0.17 percent of the maximum value excited by this wave-length; that excited by 2170A fell to 13.5 percent of the maximum value. Likewise the thermionic current decreased with outgassing. The value of φ in the Richardson equation was found to be 4.569 volts from the thermionic data for the outgassed condition, as compared with 4.57 volts calculated from the long wave-length limit measured at the same time that the thermionic data were taken. But the values of φ found by the two methods did not agree for the slightly outgassed condition. The value of φ corresponding to 3000A is 4.11 volts while the smallest value of φ from thermionic data is the value 4.569 volts. To account for this discrepancy Suhrmann assumes that photo-electrons come from the free electrons and that the decrease of photo-emission is determined more by the number of free electrons in the metal than by the work required to get an electron through the surface. His thermionic measurements show that the value of A in the Richardson equation, which is proportional to the number of free electrons, decreases from 4.76×10^{27} for the slightly outgassed condition to 1.7×10^{26} for continued outgassing. Suhrmann thinks that these results of his investigation confirm the theory of Wiedmann and Hallwachs.

Although the work of Suhrmann appears to confirm this theory in many respects, yet there are important experimental facts for which the theory does not account. These will be discussed later. Suhrmann's proof of the theory is based upon the assumption that photo-electrons come from free electrons. This assumption is contrary to our interpretation of the facts that photo-electric velocities are independent of temperature and that insulators are photo-active. Furthermore, the Compton effect,[7] which has been experimentally demonstrated, leaves little

[6] Suhrmann, Ann. der Phys. **67,** 43 (1922); Zeit. f. Phys. **13,** 17 (1923).

[7] A. H. Compton, Phys. Rev. **21,** 483 and 715 (1923); **22,** 409 (1923); P. A. Ross, Proc. Nat. Acad. **7,** 245 (1923); Becker et al., Phys. Rev. **23,** 763 (1924).

room for doubt that photo-electrons come from bound electrons. Suhrmann is led to make his assumption partly on account of the fact that a change in the value of φ of only 0.46 volt is not sufficient to account for the very great decrease in the photo-electric current that occurs as the metal is freed from its absorbed gas. Yet when the surface layer of gas is removed from a fresh specimen the increase in the photo-electric current is greater than the decrease from the maximum value as the specimen is outgassed. But the change in the long wave-length limit during the increase is not greater than it is during the decrease in the photo-electric current. Granting that the change in φ is not sufficient to account for the change in the photo-electric currents, how is this change brought about in the case of an increase when the absorbed gas is present? Suhrmann carried out his experiments under certain conditions and obtained these

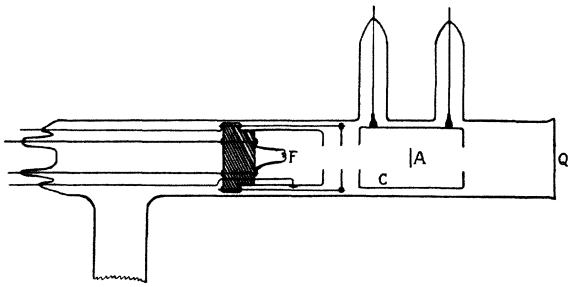

Fig. 1. Diagram of photo-electric tube.

results. Only a slight variation of the conditions would have given him quite different results. It is the purpose of the investigation reported in this paper to give results made under various conditions.

Experimental Arrangement

A photo-electric cell was made from a 40 mm Pyrex tube from which all wax and ground joints were eliminated in order to make it possible to obtain a very high vacuum. A quartz window Q (see Fig. 1) was sealed to one end of the tube with a graded seal made by the Cooper-Hewitt Electric Company. The platinum specimens A, which were ribbons 3 cm long, 0.5 cm wide, and 0.0013 cm thick, were mounted on tungsten rods sealed into glass side tubes. A copper oxide cylinder C, completely surrounded the specimen except for a hole in each end of the cylinder which allowed the incident energy to pass. The whole tube could be enclosed in an oven and baked. Mercury vapor was kept out from the experimental chamber by a liquid air trap located just outside the oven. The platinum foil could be heated by an electric current through it. The diagram shows the arrangement of the tube.

Photo-electric currents were measured with a Dolezalek electrometer which could be brought to a sensitivity of 3000 divisions per volt, if desired. Thermionic currents were measured with the electrometer or with a galvanometer. A Hilger illuminator was used for monochromatic radiation with either a mercury quartz arc, operated at constant current and constant temperature, or an iron arc as a source of radiation. A tungsten filament F was mounted inside the tube to provide a source of wave-lengths shorter than those transmitted by quartz.

The iron arc proved to be especially useful for short wave-lengths of monochromatic radiation. Using the mercury arc the photo-electric discharge excited by wave-lengths shorter than 2200A was so small that only under the most favorable circumstances could it be measured with any degree of accuracy. With the iron arc as a source of radiation, measureable deflections of the electrometer were obtained for exciting wave-lengths as short as 1850A. To be sure the radiation that passed the illuminator when the iron arc was the source was not strictly monochromatic. But, the radiation was of sufficient intensity so that the illuminator slits needed to be open not more than 0.5 mm. This gave a narrow range of wave-lengths sufficiently monochromatic for most purposes.

The unsteadiness of the iron arc is its chief disadvantage. The rate at which it radiates energy varies widely in a short time. This disadvantage was overcome by a null method of measurement suggested by Prof. Swann. The incident beam of radiation was interrupted by a small right angled quartz prism and reflected totally on to a comparison disk of platinum. The prism moved to and fro across the beam at right angles to it with a frequency great enough to ensure steady deflection of the electrometer. The beam of incident energy was reflected to the comparison disk as the prism crossed its path. At all other times the energy fell upon the test specimen. The comparison disk was connected to the insulated quadrant of the electrometer. Electrons discharged from the disk tended to neutralize the effect of the electrons fed into the insulated quadrant by the platinum specimen under test. By use of a rotating sector in the path of one of the beams the discharge of electrons from the test specimen was balanced against the discharge from the comparison disk. The area of the sector was adjusted until there was no deflection of the electrometer. The comparison disk received no treatment during the investigation and its photo-electric action remained constant. Since the energies incident upon the test specimen and upon the comparison disk were always of the same wave-length, a comparison of the photo-electric currents produced by them is allowable. The only assumption

involved is that the number of electrons discharged is proportional to the energy which strikes the metal. The angular area in the sector needed to balance the two photo-electric emissions is a measure of the emission from the test specimen in terms of the discharge from the comparison disk. This device was especially useful for determining the form of curves in the short wave-length region. The results obtained with the mercury arc always left doubt as to the shape of the curves in this region.

Results of Heating Fresh Specimens of Platinum

It is remarked by both Koppius[3] and Tucker[4] that the photo-electric current increases after the platinum has been heated for a time. Suhrmann[6] obtained a very large increase in the photo-electric current per unit incident energy by heating his platinum foil with an electric current. In all three cases the platinum was heated by an electric current through it, the method of heating used by most experimenters, if not by all, who have sought to get rid of gases.

An increase in photo-electric current was observed by the author when a fresh specimen was heated. All the specimens investigated were cleaned by dipping in nitric acid and by heating in a Bunsen flame. After mounting them in the tube none showed a detectable photo-emission when the total radiation from the mercury arc was focused upon them until after being heated by sending an electric current through them. It was not sufficient to heat them in the oven. In some cases the temperature of the baking process was as high as 500°C but in no case did the specimens become photo-active by heating in the oven at this temperature. Heating at a much lower temperature with an electric current through the specimen was sufficient to produce photo-activity. When the comparison disk of platinum, mentioned above, was mounted it gave very feeble emission when the total radiation from the iron arc was focused upon it. The Pyrex tube surrounding it was heated almost to the softening point but this had no effect upon the photo-emission from the disk. Photo-activity was increased by removing the disk from the tube and polishing off its surface with sand paper. It seems to be the experience of all investigators that an untreated specimen of platinum has some sort of layer, probably adsorbed gas, on its surface which hinders the escape of photo-electrons.

The following is a typical case of the behavior of a fresh specimen of platinum when an electric current is sent through it. In this case the tube was not baked but the pressure was reduced to about 10^{-6} mm. There was no emission under the influence of the total radiation from the mercury arc. Currents beginning with 0.1 amp. were sent through the specimen.

The currents were gradually increased with no observable effect until a current of 2 amp. was reached. Then the electrometer began to deflect. The current was kept constant, at 2 amp. and the observations plotted in Fig. 2 were made. (The deflections are in centimeters per 30 seconds observed at the times indicated.) The specimen could not have been heated by this current to a temperature higher than 250°C. This effect was noted many times with several different specimens. It was most pronounced for fresh specimens although it was also observed for specimens after the photo-electric emission had been reduced by prolonged heating. Increase in the photo-electric current is accompanied by a shift of the long wave-length limit toward the red.

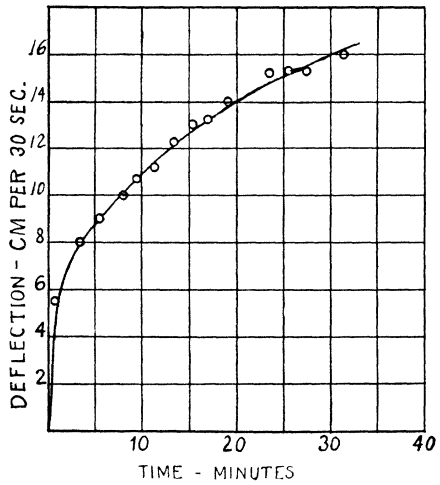

Fig. 2. Recovery of sensitivity to radiation from mercury arc while current of 2 amp. is being sent through a fresh specimen. Pressure 10^{-6} mm.

After the observations plotted in Fig. 2 were made the specimen was allowed to stand over night, the pressure being kept at about 10^{-6} mm. The next morning the rate of deflection was practically the same. When 2 amp. of heating current were sent through the specimen the deflection rose slightly to 15.3 cm. There was no further increase with time. The current was increased to 2.5 amp. and the deflection decreased. Further increase of the heating current decreased the photo-electric current gradually. When the heating current reached 4.5 amp. the deflection was but 4 cm per 30 seconds. The readings were all made with an accelerating potential of 23 volts and with the heating current flowing continuously. When the accelerating potential was reversed the specimen showed a strong discharge of positive ions coming off for heating currents greater than 2 amp. but none for heating currents of 2 amp. or less. This dis-

charge of positive ions was always found present whenever the photoelectric emission was reduced by heating the specimen.

Another specimen was tested for the same effect but in a much better vacuum. This was not a new specimen but it was newly baked to a temperature of 400°C. The pressure was below 10^{-7} mm. Beginning with 0.5 amp. the current was gradually increased to 4 amp. with no observable deflection of the electrometer. The slits of the illuminator were open 1.5 mm. At 4 amp. a slight deflection of the electrometer was observed. Readings were taken for 10 minutes. Then the slits were closed to 0.5 mm and the observations plotted in Fig. 3 were made for 2200, 2300 and 2400A. There was an accelerating potential of 14 volts. At the end of the

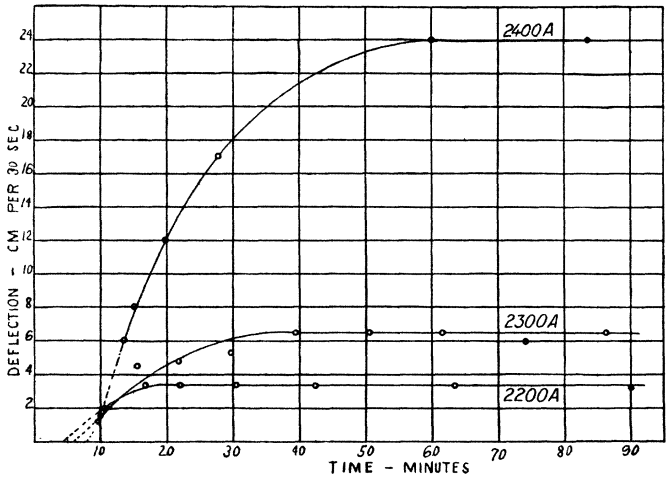

Fig. 3. Recovery of sensitivity to radiation of different wave-lengths while current of 4 amp. is being sent through specimen, previously baked at 400°C.

run the field was reversed but there were no positive ions coming off the specimen. The temperature was estimated to be about 600°C from a previous calibration curve. During the time the observations were in progress the long wave-length limit shifted from a value below that of radiation transmitted by quartz to a value of about 2550A.

The current was then increased to 4.5 amp. Immediately the photoelectric current dropped to about 80 percent of the maximum value at 4 amp. The temperature at 4.5 amp. was such that the specimen showed a just detectable faint red glow. When the current was increased to 5 amp. the emission dropped to 20 percent of the maximum value for 4 amp. Reversal of the accelerating field showed a very large emission of positive ions—much too large to be measured on the electrometer.

The Effect of Prolonged Heating on the Photo-electric Emission

One of the most pronounced effects of prolonged heating was that obtained with a specimen treated as follows: The tube was baked at 280°C for two hours. The pumps were kept running during the baking process, the pressure being about 10^{-6} mm. The specimen was then glowed 17 hours at a temperature of 1300°K. When tested for photo-electric emission there was no discharge of electrons even when the total radiation from the mercury arc was focused directly upon the specimen. This condition existed for two months. Often during this time air was admitted in to the tube to atmospheric pressure and pumped out again. Still there was no photo-emission. When the tube was filled with hydrogen and pumped out no effect was produced. Photo-activity was restored by moderate heating with an electric current.

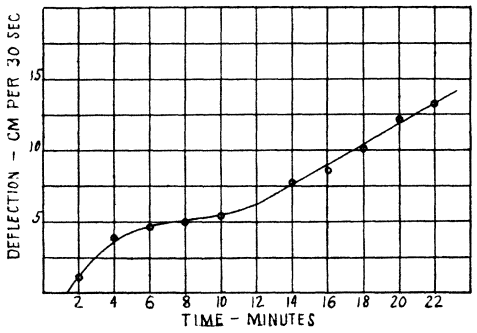

Fig. 4. Typical recovery curve for sensitivity to mercury arc radiation for specimen after prolonged heating at 1300°K. Pressure 10^{-6} mm.

The case just described is the only case in which prolonged heating caused the specimen to be inactive for such a long time. If the heating takes place at lower pressures the photo-emission disappears but returns, for the shorter wave-lengths in a few minutes, for the longer wave-lengths in a few hours at most. The time required for the return depends upon the previous history, the intensity of the heating and the duration of the heating as well as upon the wave-length of the exciting radiation and the pressure of the gas in the tube. A typical recovery curve is shown in Fig. 4. The total radiation was used for excitation. Such a curve may be repeated any number of times simply by heating the specimen for a few minutes to a moderately high temperature.

Fig. 5 shows the recovery of emission for another specimen, monochromatic radiation (2300A) being used for excitation. This specimen had been heated for 15 hours at 1300°K. The pressure during heating

was the lowest obtainable. Before the observations were begun air was admitted to a pressure of 8×10^{-6} mm. The observations were made in order beginning with the smallest heating current. The specimen was heated 5 minutes with 4 amp. of heating current (temperature about 800°K). Observations were begun as soon as the heating stopped. Immediately after the observations for the first curve were made the specimen was heated with 5 amp. (temperature about 1000°K) for 5 minutes and the observations plotted in the second curve were made. Similarly, the observations for the third curve were made after 7 amp. (temperature about 1300°K) had been used to heat the specimen. An iron arc was used as a source of radiation. The illuminator slits were open 0.5 mm. It is seen from these curves that a higher maximum is reached each time the specimen is heated. When 8 amp. were used the recovery curve was broken and irregular and after several hours the total emission had not reached the former maximum for 7 amp.

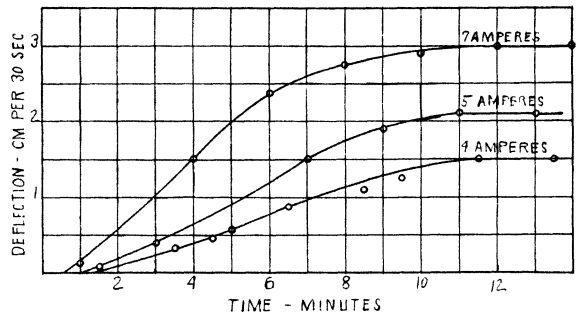

Fig. 5. Recovery of sensitivity to 2300 A (after heating for 15 hr. at 1300°K, at lowest pressure) during heating with current of 4, 5 and 7 amp. successively.

The next observations were made to test the recovery of the emission for high vacuum conditions and for different wavė-lengths. The specimen last described was used. It was rebaked and allowed to cool and baked again, the pumps running during the baking, until the pressure was too low to be registered on the ionization manometer. The observations plotted in Fig. 6 were made. The process was to heat the specimen with 7 amp. of current (temperature about 1300°K) for 5 minutes, then to make the observations immediately. Two exciting wave-lengths were used, 2400 and 2200A. An observation was made for one wavelength then the monochromator was changed to the other and an observation made for it. Thus each pair of curves represents a single recovery of emission but gives the effect with the two exciting wave-lengths. The observations plotted in the three pairs of curves were made in succession, each time the specimen being heated with 7 amp. of current for 5 minutes.

It is noted that the curves do not repeat themselves but that each time the maximum approached is a little less, the order of making the curves being from (1) to (3). This behavior is different from the behavior when the pressure is high. Then the curves can be made to repeat themselves indefinitely. Aside from the fact that there is a difference in pressure it is also to be remembered that in the case where the curves repeated themselves the specimen had been heated several hours by an electric current.

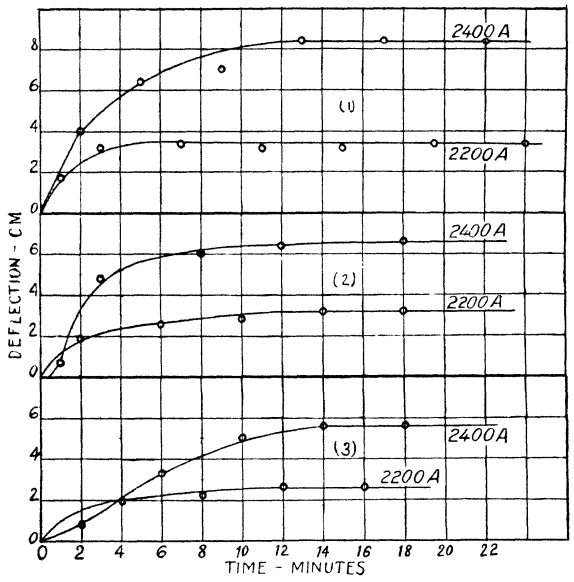

Fig. 6. Recovery of sensitivity to 2200 and 2400A, at lowest pressures, after heating to 1300°K for 5 min. The three pairs of curves were made in succession, the specimen being reheated before each pair.

The recovery curves for monochromatic radiation show that the recovery of emission occurs more rapidly for the shorter wave-lengths. This fact is emphasized particularly if the curve for the total radiation, Fig. 4 be examined. The increase in emission is still rapid after 22 minutes. Tucker[4] shows a curve plotted for a period of 2 hours in which the emission has not yet reached a maximum. The later increase in emission is that excited by the longer wave-lengths.

Still another effect of prolonged heating was observed during the latter part of the work after the best technic had been developed for obtaining a vacuum. It was found that a large change in the photo-electric current could be produced with no appreciable change in the long wave-length limit. This change in the photo-electric current was sometimes as much

as a decrease to only one seventh. This decrease in current was brought about by heating the specimen for several seconds at a temperature of about 1300°K. The emission was decreased for all wave-lengths but so far as could be detected there was no shift in the long wave-length limit. This limit was ascertained by setting the monochromator for longer and longer wave-lengths until no deflection could be observed.

The disappearance of the photo-electric emission after prolonged heating is due to the fact that the long wave-length limit has been shifted to a value below that transmitted by quartz. This was proved by mounting a tungsten filament inside the tube. The filament was properly shielded to prevent electrons getting across from it to the test specimen, being completely surrounded by a copper oxide cylinder except for an opening just large enough to allow radiation to pass. As a further precaution a copper plate was placed between the test specimen and the shield surrounding the filament. The efficiency of these devices was shown by the fact that readings taken with a magnetic field perpendicular to the line joining the filament and the test specimen agreed with those taken without the magnetic field. It was found that as the temperature of the filament was increased the radiation from it began to produce photo-emission. This test was tried on the specimen mentioned above which was so long inactive for radiation transmitted by quartz. Although there was no deflection of the electrometer under the influence of the radiation from the mercury arc, when the temperature of the filament was raised the deflection amounted to as much as 300 mm per 30 seconds.

Thermionic Measurements

Thermionic measurements were made on the specimen mentioned in the last paragraph while it was photo-electrically inactive. Before the measurements were begun the tube was newly baked out and the pressure reduced to 10^{-6} mm. The platinum foil was heated for several hours at a temperature higher than any used in the thermionic measurements. The results are plotted in Fig. 7. The value of b, in the Richardson equation, taken from this graph is 6.3×10^4. This corresponds to a long wave-length limit of 2275A if one assumes that the thermionic and photo-electric work functions are equal. After the thermionic measurements were made the specimen was still photo-electrically inactive under the influence of the total radiation from the mercury arc. However, this fact does not mean, necessarily, that the long wave-length limit of platinum was below 1850A, the shortest wave-length transmitted by quartz, for the intensity of the short wave-length energy may have been too low to give a measurable emission after the platinum had received the treatment

given it. Later investigation, using the iron arc operating on 10 to 12 amp. showed this to be the case.

Thermionic measurements were made on still another specimen. This specimen had been in use several months. It had been baked and glowed repeatedly. Before the thermionic measurements were made it had been standing under atmospheric pressure for several days. The measurements were made at as low temperatures as possible, between 1100 and 1200°K, so as to disturb as little as possible the conditions set up by the previous treatment. Currents were measured with the Dolezalek electrometer, the sensitivity being 1800 mm per volt with a capacity of about 60 cm. Just before the thermionic measurements were begun the tube was well baked and the specimen heated for two hours at a temperature of 1400°K. The pressure was kept below 10^{-7} mm.

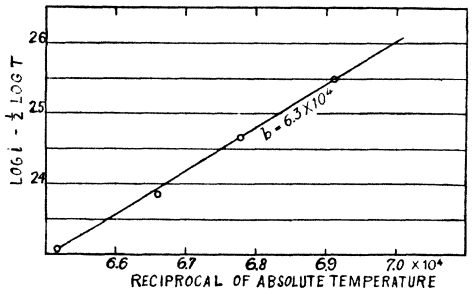

Fig. 7. Plot of thermionic measurements for photo-electrically insensitive specimen, giving value of b equal to 6.3×10^4.

The value of b as measured from the line plotted was 7.1×10^4. The specimen stood over night, the pressure remaining below 10^{-7} mm. The next morning it was glowed for one hour at a temperature of 1300°K. The thermionic measurements were repeated for the same range of temperature as the first. The value of b was 10.7×10^4. In both cases there was no photo-electric discharge of electrons immediately after the thermionic measurements were completed although the iron arc was used as the source of radiation. In the latter case photo-emission for a wave-length of 2200A was first detectable a few minutes after the heating current had been stopped. There was no emission for longer wave-lengths. The next morning the long wave-length limit had shifted toward the red so that the emission produced a deflection of 300 mm per 30 seconds for the wave-length 2400A. Other thermionic measurements at these low temperatures gave values of b abnormally high for specimens that had been heated for long periods.

These high values of b must have been due to surface conditions which were set up by the treatment given the foil. They were repeated a

sufficient number of times to ensure that they were not accidental. Each time photo-electric observations showed that there was no photo-electric emission if the foil were tested immediately after the thermionic measurements were completed. This was true even when the total radiation from the iron arc was focused on the foil. This surface condition was decidedly unstable. This is shown by the fact that if one began the measurements of thermionic current at the lowest temperature and proceeded to higher temperatures the points fell accurately on a straight line when ($\log i - \frac{1}{2} \log T$) was plotted against $1/T$, but if one returned to lower temperatures after measuring the current for higher values the points corresponding to the lower temperatures did not, in general, fall on the same line with the formerly obtained points.

Since the photo-electric long wave-length limit below 2200A could not be measured the equality of the thermionic and photo-electric work functions could not be determined. The thermionic measurements show only that whenever there is a decrease in the long wave-length limit brought about by treatment, there is a corresponding increase in the value of b of sufficient magnitude in all cases to account for the known decrease in the long wave-length limit if the equality of thermionic and photo-electric functions be assumed.

Effect of Electric Fields upon the Long Wave-Length Limit

An attempt was made to measure the velocity of the photo-electrons from a specimen that had been heated for a long period. One specimen which had been heated repeatedly was producing a deflection of 180 mm per 30 seconds with the total radiation from the mercury arc for excitation and with an accelerating potential of 30 volts. The pressure was about 10^{-6} mm. It was found that 0.06 volt was sufficient to stop all photo-electrons from the specimen. The retarding potential was increased to 2 volts. When it was removed and the specimen earthed no electrons came from the specimen when the total radiation from the mercury arc was focused upon it. When the accelerating field was reapplied the emission reappeared immediately to the full previous value. This process was repeated several times. The phenomenon was noted with several specimens. It was more pronounced with rather high pressures, that is with pressures of 10^{-5} mm, than with pressures of 10^{-7} mm, although it was present at the latter pressure. At the lower pressure there was a tendency for the specimen to remain inactive for wave-lengths above, say, 2200A. Applying an accelerating field restored the emission for the longer wave-lengths. The disappearance and restoration of the photo-

activity took place very rapidly. A double throw switch was arranged so that the change could be made from retarding field to accelerating field quite quickly. With retarding potentials as small as 0.01 volt the change could not be made rapidly enough to get a deflection of the electrometer after the retarding field was thrown on. This effect was obtained with several different specimens. It occurred only with specimens that had been heated for long periods of time, 15 to 30 hours. Tests made on unheated and slightly heated specimens did not show this effect.

Conclusion

The results of this investigation show that the initial heating of a specimen with an electric current shifts the long wave-length limit toward the red and increases the photo-electric current. This is in agreement with the results obtained by observers already quoted. The shift in the long wave-length limit and the increase in the photo-electric current may be accounted for by assuming that initially there is an adsorbed layer of gas on the surface which retards the escape of the photo-electrons. If there is such a layer of gas it may be removed by heating the platinum to a temperature of 250°C with an electric current through it. The gas is not removed by heating to 500°C in an oven. Possibly these facts may be reconciled when it is considered that all parts of the apparatus were cold when the electric current was used for heating. The gas could escape more easily than when all the apparatus was hot. Tests show that the gas discharged is not ionized.

The results of prolonged heating cannot be so readily accounted for. A first glance at the curves of Figs. 4, 5 and 6 would indicate that the Wiedmann-Hallwachs' theory is correct. Closer inspection shows that this is not the case. If the recovery of photo-activity were due to re-absorption of the gas then it should take place much more rapidly for the high pressures of Fig. 5 than for the very low pressures of Fig. 6. This is not the case. Furthermore, if the re-absorption of gas is to account for the recovery of emission the final value of the photo-electric current should depend only upon the amount of the absorbed gas. Fig. 5 shows that the final value increases as the current used to reduce the emission is raised. Fig. 6 shows that the final value is decreased as the process of heating is continued. As mentioned above, after the observations plotted in Fig. 5 were made 8 amp. were used to heat the specimen. The result was a very slow recovery which did not reach the previous maximum value after several hours. It is difficult to see how this could occur if the recovery is due to re-absorption of gas. The curves of Fig. 5 show, rather, that each time the specimen was heated more of the absorbed

and adsorbed gas was liberated. The result was an increase in the photo-electric current.

The decrease of emission to zero during the heating appears to be caused by the formation of a different sort of surface layer. The decomposition of this layer allows the photo-electric current to return, not to its former value but to a higher value which is made possible by the removal of the original gases from the surface. When 8 amp. were used as a heating current the surface layer formed was less temporary and it prevented the return of the photo-electric emission to the previous maximum value. The same sort of process is indicated by the results plotted in Fig. 6. Here as the heating is continued the final value of the photo-electric current gradually decreases. The thermionic investigation confirms these conclusions.

Further proof of the formation of some sort of retarding surface layer is furnished by the effects produced by small electric fields. An electric field could not remove or deposit, instantaneously, a layer of gas, but it could alter the arrangement of an ionic layer on the metal surface so as to make it a retarding influence.

Large decreases or increases of photo-electric current with no change in the long wave-length limit, or with insufficient change to produce the variation in the photo-electric current, may be accounted for by the formation of the retarding layer in patches on the surface of the platinum. Other areas are uncovered and continue to emit with the same or with little changed long wave-length limit. Thus the total photo-electric current is reduced but the long wave-length limit remains constant. This condition occurred in the author's investigations only when the gas pressures were the lowest. This fact would indicate that the retarding layer is formed from the residual gas in the tube. When the pressure is very low there may not be sufficient gas to form a layer which completely covers the surface of the metal.

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