CHANGES IN THE PHOTO-ELECTRIC THRESHOLD OF MERCURY

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Abstract

Photo-electric threshold for the clean surface.—C. B. Kazda has found the photo-electric threshold of a mercury surface cleansed of impurities by means of a constant overflow. In the present work his value of 2735A for the threshold of clean mercury is checked.

Changes in photo-electric threshold of Hg. that take place in a high vacuum.—When the surface flow is allowed to stop in a high vacuum, some impurity attacks the surface, quickly raising the threshold to 2850A. If liquid air is not used, this impurity is present in larger amounts and attacks the running surface. Indications are that a surface film is formed and maintained in spite of the flow when liquid air is not used, or requires two hours or more for removal if liquid air is used. This impurity can not be one of the gases with extremely low melting points. It is not water, but may be a component of the stopcock grease. When the surface is left standing several days in a high vacuum, its threshold falls to 2680A. If liquid air is not used, the standing surface has a limit of 2560A. All of these values are closely reproducible.

Indirect effect of hydrogen on the photo-electric threshold of Hg.—Pure hydrogen in contact with the surface does not change the photo-electric behavior. When the mercury is condensed in the presence of hydrogen, some of the gas is dissolved in the metal. This does not change the characteristic threshold of the mercury. It does, however, have the effect of greatly impeding the action of other impurities that form on the surface. This is indicated by the fact that over two hours is required for the change from the threshold of 2735A for the clean surface to the maximum of 2580A, as compared with 13 minutes for this change when hydrogen is not present.

THE photo-electric threshold for mercury has been found by Kazda[1] at 2735A. He was able to eliminate all effects of impurities by making his measurements on a flowing surface. This was probably the first time that a clean surface of metal had been used in photo-electric experiments, with any degree of certainty, and it was thus possible for him to demonstrate that a metal does possess a definitely characteristic threshold. At the same time, the clean surface offers the best possible starting point for an investigation of the effect of impurities on the threshold. It was for the latter purpose that the work reported in the present paper was undertaken.

Apparatus and Method

The experimental arrangement was, in the main, just as it was used by Kazda. The reader is referred to his paper for a diagram of the apparatus and a more detailed account of the experimental method. Briefly, the surface flow was realized by operating a mercury still and allowing the condensed mercury to overflow from a cup inside the photo-electric cell. The source of light was a quartz mercury arc, and a monochromatic illuminator was

[1] C. B. Kazda, Phys. Rev. **26**, 643 (1925).

arranged to direct light of any desired wave-length onto the mercury surface. The relative intensities of the lines of the arc were measured by means of a delicate thermopile, in vacuum. The photo-electric effect of any given wave-length was measured by a quadrant electrometer by the usual rate of deflection method. The photo-electric effect per unit intensity was then plotted as a function of the wave-length, and the intercept with the wave-length axis gave the threshold, with an uncertainty of not more than ± 10A. When it was desired to follow rapid changes in the sensitivity the rate of deflection method was too slow. In such cases a constant deflection method was used, the quadrants connected to the photo-cell being shunted to the ground by a radioactive leak.

The Threshold for the Flowing Surface

The value found by Kazda for the long wave-length limit of the flowing surface of mercury was 2735A. In more than a dozen determinations in the present work, this limit was always found between 2735A and 2750A. It

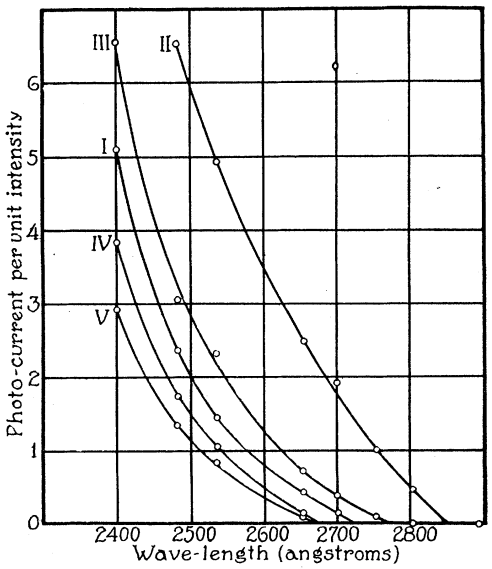

Fig. 1. Change of threshold of mercury. I. Curve for flowing surface. II. 13 minutes after turning off still. III. 18 hours after turning off still. IV. 66 hours after turning off still. V. 114 hours after turning off still.

must be noted too, that the higher values were obtained under less favorable conditions, i. e. less prolonged pumping and running of the still since the last contamination of the surface. A curve for the clean surface is shown at I, Fig. 1.

Stationary Surface in High Vacuum

Curve I, Fig. 3, shows the changes that take place in the sensitivity to the line 2653A, when the clean surface is exposed to a vacuum of the order

of 10^{-6} mm of mercury. Before this experiment was started the surface had been flowing for some time and showed the normal threshold of 2735A. The sensitivity was constant. At the time marked zero the still was turned off. The surface flow immediately slowed down, and in about ten minutes stopped altogether. As may be seen from the curve, the sensitivity to 2653A rose to a maximum of about five times that when running, about 13 minutes being required for the rise. The sensitivity then began to decrease, rather rapidly for about 40 minutes, then more slowly. This slow fall continued over several days.

Fig. 1 shows the threshold curves for the changing surface. Curve I is for the flowing surface, and gives 2735A for the threshold. Curve II is for the highest point reached after stopping the flow, i. e. about 13 minutes after turning off the still. The limit given is 2850A. Curve III was taken after 18 hours of standing, the limit having now fallen to 2770A. Curve IV was taken after 66 hours, and V after 114 hours. Both show a threshold of about 2680A, indicating that a constant value has been reached. It is to be noted that the threshold first rises some 115A above that for clean mercury, but eventually drops to 55A below that value. It should be explained that curve II was not taken all in one run, as were the others, for the reason that the surface does not remain in the most sensitive condition long enough for a threshold curve to be taken. It was obtained by successively running curves like I, Fig. 3, for the different lines of the arc, the highest point of each being used for plotting the point of II, Fig. 1, for that wave-length.

From a study of these results it would seem that there are at least two stages to the process of contamination of the surface. This might be attributed to two different impurities, one acting very quickly and raising the threshold, the other lowering it, but acting much more slowly. It is more likely that one agent is responsible for both phenomena, a single layer of molecules assisting the release of electrons, but greater thicknesses tending to stop the slower electrons and thus lower the threshold. This is in accord with the results of Becker[2] on the thermionic work function of platinum covered with caesium.

Contamination by Removal of Liquid Air

Marked changes in the long wave-length limit and sensitivity took place when the liquid air was removed from the trap connected with the apparatus. When this was done with a surface that had been standing for some time in a high vacuum, a drop in the threshold occurred. For example, the surface had been standing in a high vacuum for 46 hours, and showed a threshold of 2785A. With the pumps running continuously, the liquid air was removed. An immediate drop in the sensitivity to the 2653 line was noticed, and after two hours time it had fallen to zero. A threshold curve then showed the limit to be 2570A. This curve is shown at I, Fig. 2. After 20 hours curve II was taken. The limit had remained practically the same, falling perhaps to 2560A. The sensitivity, however, especially for $\lambda = 2400$A,

[2] J. A. Becker, Phys. Rev. **28**, 341 (1926).

had decreased considerably. This value of 2560A was obtained repeatedly, and may then be taken as characteristic of standing mercury contaminated by something that is released when the liquid air is removed. After curve II was taken, the liquid air was replaced, and after 22 hours the threshold was found to have risen to 2600A, the surface not having been disturbed meanwhile. This was repeated on another occasion, the limit 2600A being observed after the liquid air had been replaced for 56 hours.

On one occasion a slight rise in sensitivity was first observed when the liquid air was removed. The surface had been standing for only a few hours, and had the limit 2830A. The deflection for $\lambda = 2653$A was 253 mm. When

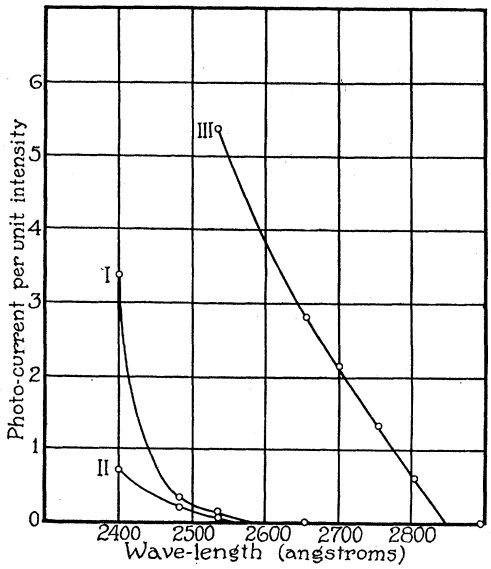

Fig. 2. Effect of removal of liquid air on the threshold. I and II. Curves for standing surface. III. Curve for flowing surface.

the liquid air was removed it rose in six minutes to 272 mm, then proceeded to drop in the usual manner. The threshold reached the value 2560A in two hours time.

When the liquid air was removed while the surface was running, nothing happened until the trap reached such a temperature that the frost began to disappear from its outside. Then, however, a sharp rise in sensitivity was noticed, while the threshold rose from the usual 2735A to the value 2850A. The curve is shown at III, Fig. 2. The rate of flow was increased until the surface was too turbulent to permit consistent results, but no change in this value was obtained. After the liquid air was replaced, several hours of pumping and running the still were required to bring the threshold back to normal. Repetition of the experiment gave identical results.

It thus appears that there is some impurity that can attack even the flowing surface if present in large enough concentrations. Furthermore, it seems probable that this is the same impurity that causes the highest

sensitivity of the surface standing in a high vacuum, since the same threshold, 2850A, was observed in both cases. When liquid air is used, the concentration of this impurity is not high enough to permit its attacking the flowing surface.

While the highest values reached by the threshold are identical, there is a difference in the lowest values reached by the standing surface, with and without liquid air. In the former case, there is a definite tendency to stop at 2680A, while in the latter case the limit falls to 2560A.

The impurity responsible for the threshold of 2850A would seem to be something whose vapor pressure increases rapidly in the neighborhood of 0°C. To test whether or not it is water vapor, a side tube containing a little water was sealed to the apparatus between the liquid air trap and the photocell, and immersed in liquid air. Liquid air was also kept on the regular trap. The apparatus was exhausted and the mercury surface brought to its normal running behavior. The 2653 line gave a deflection of 178 mm. The liquid air around the water was then replaced by brine at -20°C. The deflection began to fall very slowly, reaching 125 mm after $2\frac{1}{2}$ hours. The brine was then removed, and the fall was more rapid, the deflection going to 92 mm in about 14 minutes. The liquid air was replaced, and the deflection rose in 9 minutes to 174 mm, close to its former value. At no point was any rise in sensitivity noted due to the release of the water, in spite of the fact that the brine was used to insure a very slow release at first. This result is not necessarily inconsistent with that of Kazda, who found that small amounts of water vapor cause a rise in the threshold of a standing mercury surface, for here the experiment was made with a flowing surface.

Since stopcocks were used as a part of the apparatus, it is evident that vapor from the stopcock grease must have been condensed in the liquid air trap. A side tube containing a small quantity of the grease was sealed to the apparatus, and treated in the same manner as the water had been (except that brine was not used). With pumps running and surface flowing, the liquid air was removed from the grease, while that on the regular trap was kept in position. This time the rise in sensitivity and threshold was observed, the latter reaching and holding the value 2850A quite exactly. While these tests are not entirely conclusive, it is very probable that some component of the grease is responsible for many of the changes observed.

Hydrogen in Contact with the Surface

Extensive tests were made with hydrogen in contact with the mercury surface. The hydrogen was purified, and admitted to the apparatus at pressures ranging from 10^{-4} to 10^{-1} mm, and tests were made both with the standing surface and with the surface flowing at various rates. Observations were also made of the changes taking place when the surface flow was allowed to stop. In all cases the behavior was exactly as when the hydrogen was not present, with the exception that when the pressure exceeded 10^{-3} mm a slight decrease in the photo-current was noticed. This was undoubtedly a space, not a surface, effect, for it was roughly proportional to the pressure, and the same effect was observed when air was used instead of hydrogen.

We must conclude that pure hydrogen does not modify the surface in a way that affects the photo-electric behavior.

Hydrogen Present in the Still

Suhrmann[3] has proposed a theory that in an electron emission of any kind from a metal, a gas dissolved in the metal has the effect of increasing the emission, while an adsorbed layer of gas on the surface decreases the emission. An experiment was devised to test this theory, and, while it failed to confirm the theory, an interesting effect was discovered.

The apparatus had been constructed in such a manner that the still was connected with the photo-cell only by two small tubes. One of these contained the condensed mercury flowing to the cell, the other contained the overflow from the cell, running back to the bottom of the still. Since both tubes were full of mercury, a pressure of several centimeters could be

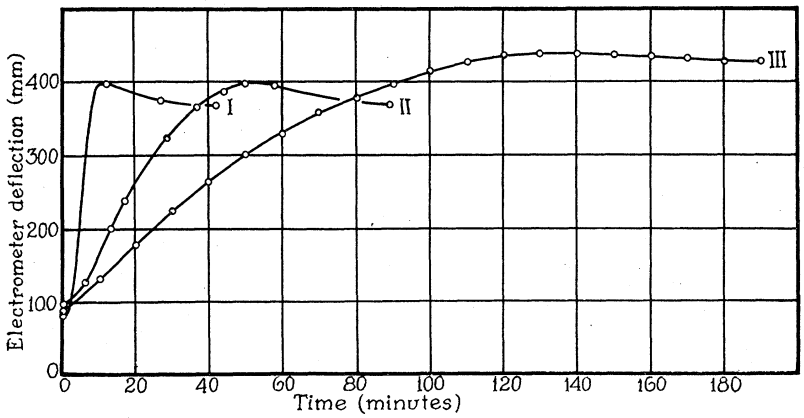

Fig. 3. Rise of sensitivity after stopping surface flow. I. Curve taken in high vacuum. II and III. Taken with hydrogen in the still.

maintained in the still without affecting the pressure in the cell. The two parts of the apparatus were connected to the same pumps, but could be separately closed off by means of large mercury-sealed stopcocks. A separate liquid air trap was provided for each branch. It was then possible to admit hydrogen to the still, while a high vacuum was maintained in the photo-cell.

With the still running, hydrogen was admitted to it, to a pressure of 8 mm. It was thought probable that some of the hydrogen would dissolve in the condensing mercury, and flow with it through the small tube to the photo-cell. An increase in emission would then occur if Suhrmann were right. No such increase in emission was observed, although the electrometer deflection was carefully watched for more than two hours, during which time the small tube leading to the cell must have emptied many times. No change in the sensitivity or threshold of the flowing surface occurred.

[3] R. Suhrmann, Zeits. f. Tech. Physik, **4**, 304 (1923).

When, however, the still was turned off and the surface flow allowed to stop, *the time required for the rise to maximum sensitivity was 49 minutes.* Two days previous, this time had been 12 minutes. In the year preceding and the two months following the experiment described here, this time of rise was observed under high vacuum conditions some 27 times, and always found to lie between 11 and 20 minutes. The 20-minute rise had been observed on only one occasion, the most common value being 13 minutes. The 49-minute rise was then a radical departure in behavior. It is shown in curve II, Fig. 3, where it may be compared with I, taken without hydrogen present. It is noticed that the highest sensitivity is practically the name, the only difference being the introduction of a time factor.

Curve I, Fig. 4, is the threshold curve for the flowing surface, either with or without hydrogen present in the still. Curve II was taken when the highest

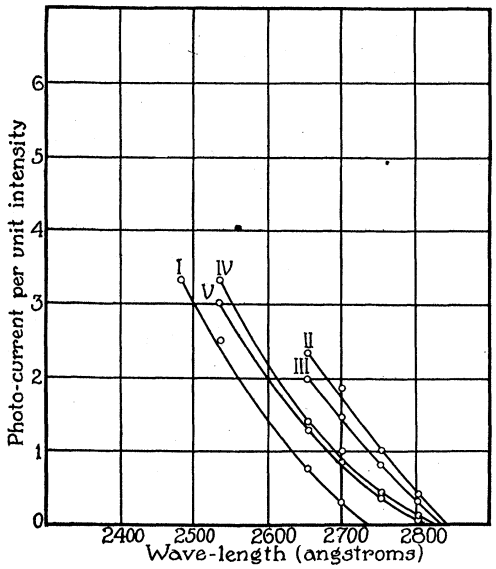

Fig. 4. Change of threshold with hydrogen in the still. I. Curve for flowing surface. II. 50 minutes after turning off still. III. 14 hours after turning off still. IV. 85 hours after turning off still. V. 110 hours after turning off still.

sensitivity had been reached, 50 minutes after turning off the still. The threshold shown is 2850A, the same as that reached when hydrogen is not present. The surface was then left standing, and curves III, IV, and V were taken after 14, 85, and 110 hours, respectively. If these are compared with the curves of Fig. 1, obtained similarly but without hydrogen present in the still, it is seen that the rate of fall of the threshold is now much less.

After curve V of Fig. 4 had been taken, the still was again started, the hydrogen being allowed to remain. After two hours of running, the normal threshold of 2735A was obtained. The time of rise after turning off the still was 44 minutes. The next day a repetition of the experiment gave 84

minutes, while three days later 124 minutes was required. This last result is shown in curve III, Fig. 3. In all cases the threshold reached the maximum of 2850A.

The hydrogen was then pumped from the still, the pumping being continued for several days and the still operated at the same time, in order to free the mercury from hydrogen as completely as possible. The time of rise was then found to be 20 minutes. Two weeks later it had fallen to 14 minutes. A second admission of hydrogen to the still increased the time again to 122 minutes, checking the former result.

From this behavior we may draw three conclusions: first, hydrogen does dissolve appreciably in the mercury and flow with it to the photo-cell; second, this dissolved hydrogen does not change the threshold of the clean running surface; third, the action of some other impurity is greatly impeded by the presence of the hydrogen. The explanation of this third result would seem to be that the hydrogen evaporates from the mercury surface and diffuses away from it, resulting in a lowering of the pressure of the other impurity in that vicinity.

The possibility of such an indirect effect of hydrogen, and perhaps of some other gases, should be considered in connection with many other photo-electric experiments. For example, Dümpelmann and Hein[4] have found that the photo-electric sensitivity of a metal plate is increased when either hydrogen or oxygen is generated electrolytically on the other side of the plate. It is probable that this is due, not to any direct effect of the gas upon the photo-electric properties of the metal, but rather to the driving away, by the gas diffusing through the plate, of some other impurity that has been holding down the sensitivity.

In conclusion, I wish to express my warmest thanks to Professor R. A. Millikan for his direction of the work here reported.

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September 30, 1926.

[4] R. Dümpelmann and W. Hein, Zeits. f. Physik, **22**, 368 (1924).