THE EFFECT OF SURFACE MODIFICATIONS ON THE PHOTO-ELECTRIC THRESHOLD OF MERCURY

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Abstract

This work is a continuation of that of Kazda, who found the long wavelength limit of a mercury surface cleansed of impurities by means of a constant overflow.

Kazda's value of 2735A for the threshold of clean mercury is checked. 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 of flow 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. 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 2850A, as compared with 13 minutes for this change when hydrogen is not present.

1. Introduction.

In November, 1923, Dr.C.B.Kazda[1], working in this laboratory, completed an investigation of the photoelectric threshold of mercury. Dr.Kazda was able to eliminate all effects of impurities by making his measurements on a flowing surface. Thus he obtained the threshold for pure mercury with greater certainty than had been done before for any metal. At the same time his results furnished evidence that a pure metal does exhibit a photoelectric effect. This is contrary to the view held by Hallwachs, Fredenhagen, and others, that the photoelectric effect in metals depends for its existence upon the presence of impurities. I shall show later that Kazda's evidence is not quite conclusive on this point. It is, however, very strong indeed.

It was evident at once that Kazda's arrangement offered an excellent opportunity for modifying the metal surface and observing the resulting changes in photoelectric sensitivity and threshold value. This phase of photoelectric behavior - the variations that take place with different treatment of the surface - has perhaps undergone more investigation than any other. Yet the fundamental processes involved and the agents actually responsible for the changes have in most cases remained undetermined. These things are exceedingly elusive, even though their effects are very apparent, as everyone who has worked in this field knows. It was to obtain some additional data in this regard that the present investigation was undertaken.

2. Apparatus.

The experimental arrangement was, in the main, just as it was used by Kazda. I shall

1. C.B.Kazda, Doctor's Thesis, Cal.Inst.Tech., 1924.

describe it again here briefly.

Referring to fig.1, the photoelectric cell is seen on the left, a mercury still on the right. The mercury is evaporated at a rate which depends on the current supplied to the heater. It recondenses inside the water jacket and falls into the tube below, the fall being broken by a perforated glass plate. The mercury then flows through the small tube and up into the small iron cup, where it presents a surface. It then overflows down the inclined iron tube, and returns to the still. Above and around the iron cup is a cylinder of oxidized copper, closed above except for a slit to admit the light. This receives the electrons driven from the mercury surface, and is connected by shielded wire to the electrometer. The mercury is maintained at a negative potential with respect to the ground, three volts being sufficient to obtain saturation. Above the receiver the cell is closed by a quartz window to admit the ultra-violet light. The apparatus, except where I have made other mention, is constructed of pyrex glass. The photoelectric cell and the tubes leading to it from the still are covered with grounded tinfoil, to prevent the charges carried by the condensing mercury from inducing charges in the electrometer system. Both still and photocell are connected through liquid air traps to two stages of Langmuir condensation pumps, these being supported by a Cenco Hyvac pump.

The source of light is a quartz mercury arc, enclosed in an asbestos-lined box. By means of a camera shutter light from the box is allowed to enter a Hilger monochromator, from which it passes through a quartz lens and is focused upon the slit in the receiver. Thus it falls vertically upon the mercury surface, without touching the copper oxide receiver.

The relative intensities of the lines of the arc are measured by means of a delicate vacuum

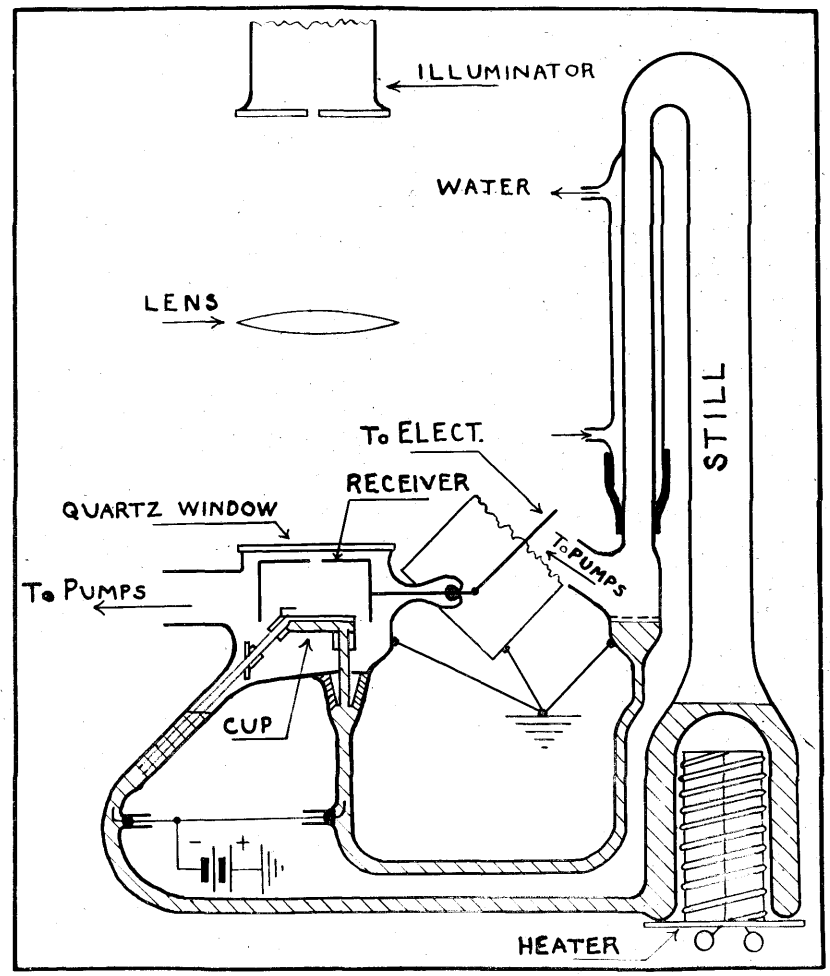

Fig. 1. Apparatus.

thermopile, connected to a high-sensitivity galvanometer. This thermopile is pictured and fully described in Kazda's paper. In the latter part of my own work the thermopile of four couples, as used by Kazda, was replaced by a single couple of similar construction, the light being brought to a smaller focus by means of an added quartz lens of short focus placed just above the cell containing the couple. This had more mechanical stability than the old arrangement, and gave very similar results.

The Dolazalek electrometer used in measuring the photocurrents had a sensitivity of 1060 mm. per volt on a scale at 150 cm. distance, with 129 volts on the needle. In finding the threshold values, the monochromator was set to transmit a given line of the mercury spectrum. The ground to the electrometer quadrant was then removed, and as soon as the needle was steady the shutter admitting light to the monochromator was opened and left open long enough to produce a sizable deflection. The exposure was timed by a seconds pendulum operating a sounder on the observing table. After closing the shutter the needle was allowed to come to rest and the reading taken. This was then corrected for the leak that occurred during the time required for the reading. This leak was of the order of five mm. per minute, and was fairly constant, but for safety it was determined after every reading. Successive readings with the same line could be checked to within two or three mm. With a deflection of 100 mm., such as was often obtained, the accuracy was then two or three percent. This varied slightly with the rate of charge. When readings had been taken for several lines near the threshold, the readings were reduced to equal times of exposure and each divided by the corresponding intensity. The photocurrent per unit intensity was then plotted against the wavelength, and the intersection with the wavelength axis gave the photoelectric threshold. The currents, as photocurrents go, were quite large, and the intensities

accurately determined. This enabled me to use a large scale on the photocurrent axis and still get smooth curves. In this way sharp intersections with the wavelength axis were obtained, the uncertainty being not more than 10A on either side of the chosen point, in most cases.

Readings taken in the above manner required from two to three minutes each, and hence were not satisfactory for observing rapid changes in sensitivity. A constant deflection method is more desirable, and for this purpose a radioactive leak was connected to the electrometer. This leak, together with the other electrometer connections, is shown in fig.2. The leak occurred between the central cylindrical electrode and the outer cylindrical case, the air between them being ionized by the radiation from some uranium oxide (U_3O_8) on a plate at the left side. The value of the resistance thus shunted across the electrometer could be varied by moving the plate carrying the U_3O_8. This resistance did not follow Ohm's law accurately enough to be used in taking thresholds, so these were always taken by the rate of charge method. The radioactive leak does possess the decided advantage, however, that its resistance remains the same over long periods of time, and so readings taken days or weeks apart may be compared, equal readings meaning equal currents. The leak could be easily disconnected, leaving the electrometer free for the other type of reading.

The mercury used for the observations had been carefully cleaned, and distilled several times in the presence of a small amount of air. In this way the more volatile elements were oxidized and then removed in later distillations. It may be safely assumed that no impurities were present in large enough concentrations to affect the photocurrents, except those impurities that form directly on the surface from the gases in contact with it.

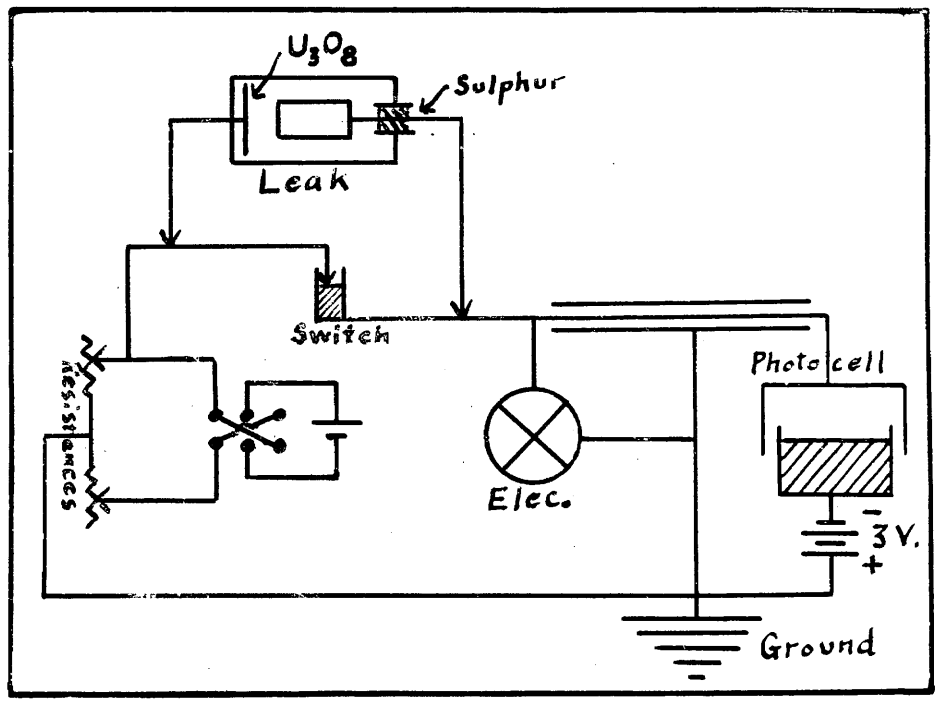

Fig. 2. Electrometer Connections.

3. The Threshold For The Flowing Surface.

The value found by Kazda for the long wavelength limit of the flowing surface of mercury was 2735A, or 2745A when slight corrections were made for stray light. In more than a dozen determinations of my own, this limit was always found between 2735A and 2750A. It 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. Under the best conditions the threshold found was always close to 2735A. A sample curve is shown in I, fig.5, the data for it being given in the table below. The small deflections for 2754A and 2803A may be accounted for by stray light of other wavelengths. As mentioned above, the uncertainty in locating the intercept of such a curve on the wavelength axis is surely not more than 10A. Thus Kazda's value for the threshold of clean mercury has been checked, though this check may be discounted somewhat by the fact that it was obtained on the same apparatus.

Wavelength, Angstroms	Deflection in 8 sec., mm.	Relative Intensities
2400	16.4	31
2482	22.8	95
2537	53.0	362
2653	12.1	283
2700	.96	60
2754	.12	49
2803	.03	146

Data for Curve I, fig.5.

4. Stationary Surface In High Vacuum.

Assuming that the surface flowing in a high vacuum is perfectly clean and that the effects observed under these conditions are then definitely characteristic of mercury, it is important next to investigate the difference

in behavior when the surface is stationary, the high vacuum being maintained. With a perfect vacuum one would expect the behavior to remain unchanged. In my experiments the vacuum was a little better than could be measured with the McLeod gauge, which means it was probably about 10^{-6} mm of Hg. This is of course by no means perfect, hence contamination is to be expected.

Fig.3 shows the changes that take place in the sensitivity to the line 2653A, as the surface is allowed to stop. Before this experiment was started, the surface had been running 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 nearly five times that when running, about 18 minutes being required for the rise. The sensitivity then began to decrease, rather rapidly for about 50 minutes, then more slowly. This slow fall continued over several days.

In fig.4 the opposite process is pictured. The surface had remained standing for several days, and the sensitivity to 2653A had fallen to a low value. At time zero the heater for the still was turned on. About 15 minutes elapsed before the distillation began, but as soon as the surface was broken by the first flow, the sensitivity quickly rose to a high value. It then began to fall, and did not approach constant behavior until after two hours. The spread of points in the descending portion is not due to error in reading the electrometer deflections, but shows actual fluctuations in the sensitivity. This is due to the more intermittent character of the flow before the still is fully warmed. The still does reach steady flow, however, some time before the sensitivity

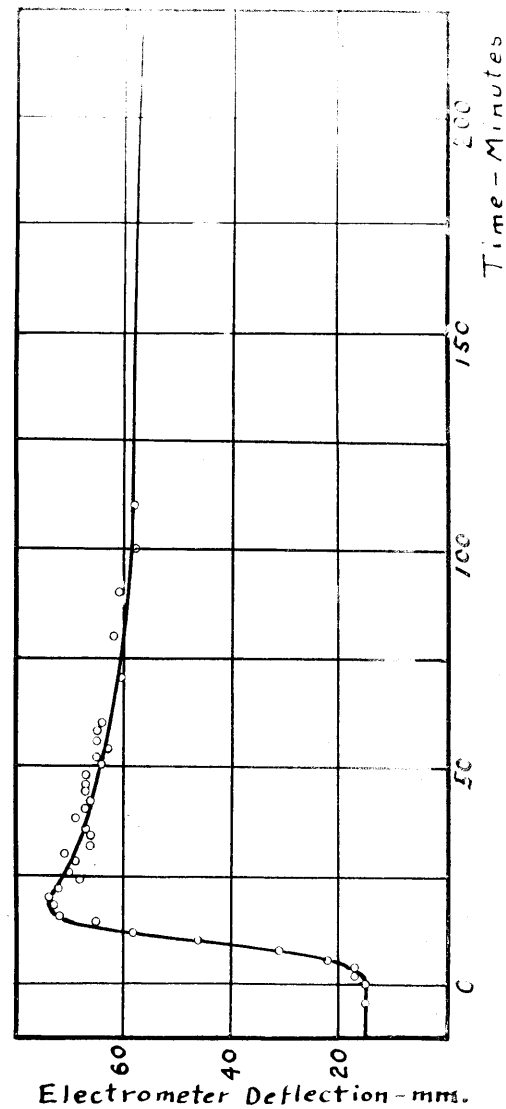

Fig. 3. Change of sensitivity to λ=2653A, with surface flow stopping.

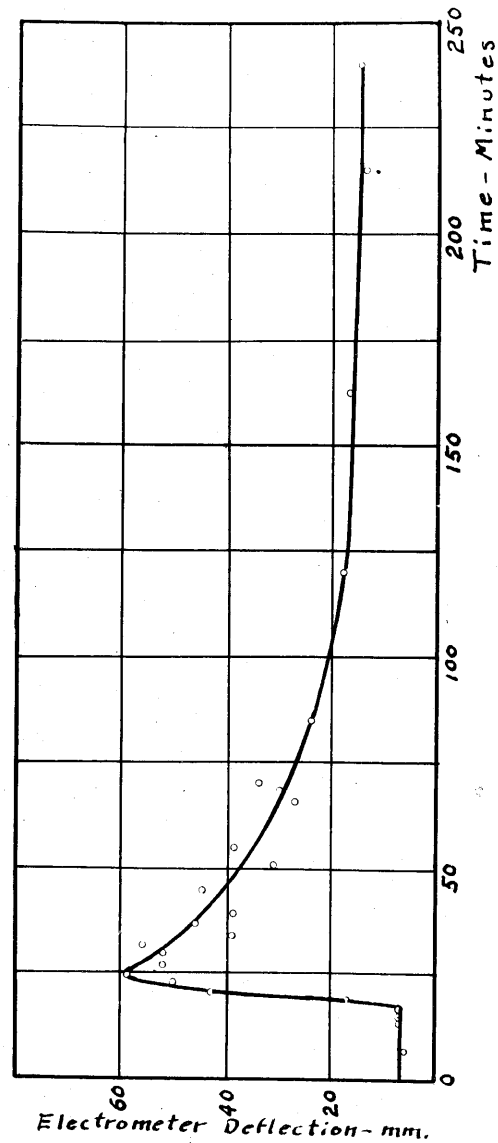

Fig. 4. Change of sensitivity to λ=2653A, with surface flow starting.

becomes constant. This was shown conclusively in later experiments where the surface had been given a better chance for contamination, and as a consequence five hours or more of running was necessary to bring the sensitivity down to normal. A higher rate of flow results in reaching constant behavior more quickly.

Fig.5 shows the threshold curves for the changing surface. Curve I is for the running surface, and gives 2735A for the threshold. Curve II is for the highest point reached after stopping the flow, i.e. from 12 to 18 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 the flowing surface, but eventually drops 55A below that value. It must 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 that of fig.3 for the different lines of the arc, the highest point of each being used for plotting the point of II, fig.5, for that wavelength.

From a study of figs. 3 and 5, it would seem that there are at least two stages to the process of contamination of the surface. Two different impurities may be responsible for this, the one acting very quickly and raising the threshold, the other lowering it but acting much more slowly. Or it may be 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

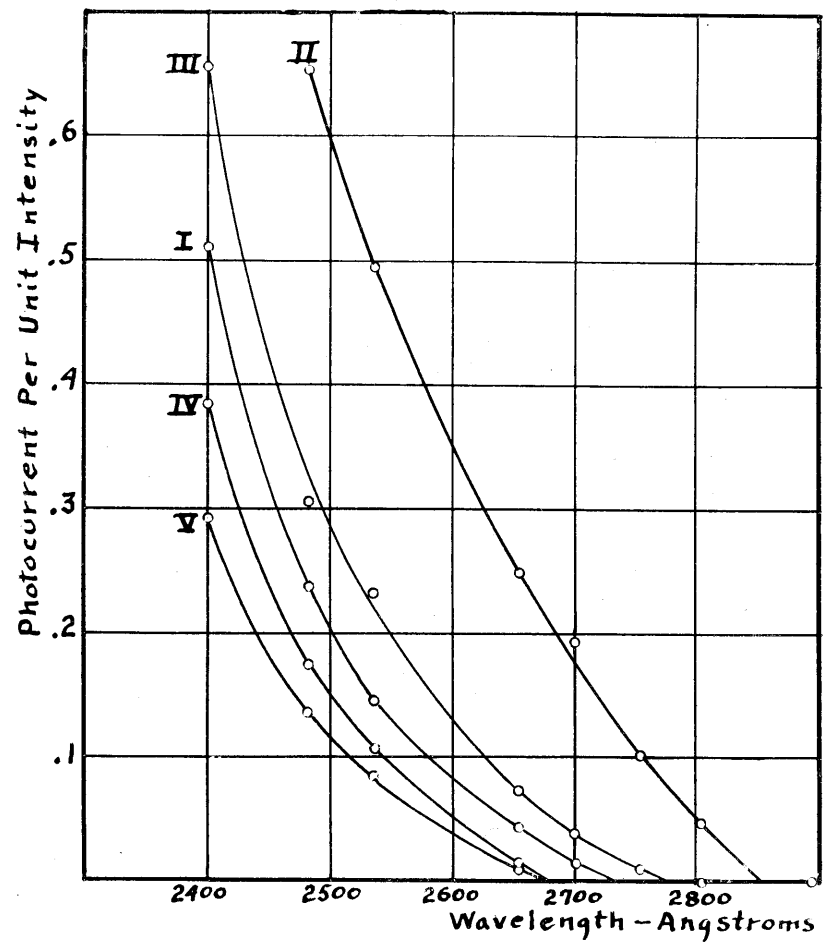

Fig. 5. Change of Threshold.

I	Curve for flowing surface.
II	13 minutes after turning off still.
III	18 hours " " " "
IV	66 " " " " "
V	114 " " " " "

and thus lower the threshold. Whichever of these is correct, it is evident from fig.4 that the second stage of contamination is quickly removed when the surface is broken, while the other holds more tenaciously. It would seem that a film is formed over the surface, and that this is only gradually broken up and carried away by the flow. That it is at last completely removed, however, is seen from the fact that a constant reproducible value of the threshold is finally reached, this value being independent of the rate of flow of the surface.

5. Removal Of Liquid Air.

It was next necessary, of course, to depart from the high vacuum condition. One of the simplest ways of doing this was to remove the liquid air from the trap connceted with the photocell. This was done at first only with a surface that had been standing some time in a high vacuum. What was nearly always observed was an immediate drop in both sensitivity and long wavelength limit, the latter reaching a value of 2560A. For example, the surface had been standing under a high vacuum for 46 hours, and showed a threshold of 2785A. The deflection for the 2653 line was 80 mm. With the pumps running, the liquid air was removed. In about two hours time the deflection for 2653A had fallen to zero. A threshold curve was taken, giving the value 2570A. This curve is shown at I, fig.6. After 20 hours curve II was taken. The limit had remained practically the same, falling perhaps to 2560A. The sensitivity, however, especially for λ=2400A, 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 liquid air was replaced on the trap, and after 22 hours the threshold was found to have risen to 2600A,

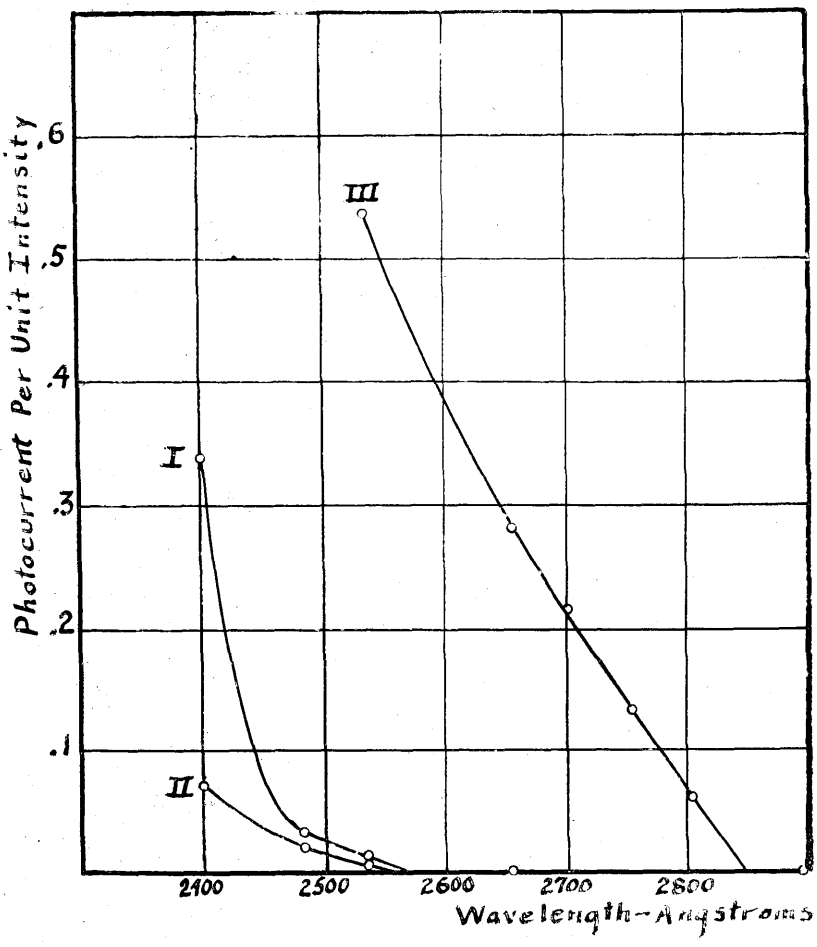

Fig. 6. Removal of liquid air.

I and II, Standing surface.
III, Flowing surface.

the surface not being disturbed meanwhile. This was repeated on another occasion, the limit 2600A being observed after liquid air had been on for 56 hours.

I have stated above that an immediate drop of sensitivity was usually observed when the liquid air was removed. On one occasion, however, a slight rise was observed before the drop. The surface had been stationary for a few hours, the limit being 2830A. The deflection for λ=2653A was 253 mm. When the liquid air was removed it rose in 6 minutes to 272 mm, then proceeded to drop in the usual manner. The limit reached the value 2560A in two hours time.

The effect of removing the liquid air while the surface was running was next investigated. I expected no changes to occur on doing this, counting on the ability of the running surface to keep itself clean. The result, however, was not as expected. The surface, prior to the removal of the liquid air, was behaving in the normal manner, having a limit of 2750A. The sensitivity to 2653A was 115 mm. When the liquid air was removed, nothing happened until the temperature of the trap became high enough that the frost on its outside began to melt. Then the sensitivity quickly rose to 392 mm and remained there. A considerable increase in the rate of surface flow, such that the surface could be seen to be violently agitated, did not change this value. The threshold was then measured and found to be 2850A. The curve is shown at III, fig.6. The pumps were operated continuously during this experiment. It was found that after replacing the liquid air, three days of pumping and running the still were required to bring the surface back to normal behavior. The whole operation was repeated at another time with results that checked almost identically with those given above.

It is this result that throws some doubt on Kazda's claim for a clean surface. His claim is based chiefly on the fact that constant, reproducible results are obtained, independent of the rate of flow when this is fast enough, together with the common sense opinion that a surface in contact with the vacuum for so short a time had no chance to become contaminated. In the present experiment a constant, reproducible value of the threshold was obtained, which was independent of the rate of flow, but was different from that when liquid air is present. There is some chance, then, that Kazda's running surface may have been modified by some rapidly acting impurity, just as it evidently is when the liquid air is removed. The same impurity can not be responsible for both values, however; for, when the liquid air is replaced the threshold gradually returns to Kazda's value and remains there. This shows that the impurity released by the removal of the liquid air has been entirely removed. The second notion, - that the surface must be clean on account of its short exposure to the vacuum, - can of course be applied with much greater certainty to the case where liquid air is used, for there the vacuum is much better. In view of this it still seems most probable to me that Kazda's surface was quite clean.

It is almost certain that the impurity responsible for the changed threshold of the running surface, is the same as that which causes the rise in sensitivity when the surface flow is stopped in a high vacuum. In the experiment described above, the sensitivity to 2653A rose from 115 to 392 on the removal of the liquid air. On the previous day, the surface had been allowed to stop in a high vacuum, and the sensitivity rose from 100 to a maximum of 387. In addition, the threshold of 2850A found here is identical with the highest point reached by the

threshold on stopping the surface, as given by curve II, fig.5. When liquid air is used this impurity is not present in large enough quantities to attack the running surface, but does quickly form a film on a standing surface. When the liquid air is removed it attacks the running surface.

We are unable to say whether the fall in threshold value for the standing surface when the liquid air is removed is due to a different impurity, or to an excess of the same one that causes the rise on the running surface. It does not seem to be the same as that which causes the fall of the limit for the surface standing several days in a high vacuum, for the latter showed a tendency to stop at 2680A, while the removal of liquid air causes the limit of the standing surface to fall to 2560A.

The agent responsible for the threshold of 2850A is evidently not one of the gases with very low melting point, since it did not begin to have an effect until the temperature of the trap rose to near 0°C. Water vapor seemed the most likely, especially since Meyer[2] has found that small quantities of water vapor lower sparking potentials, while larger amounts cause an increase. To test this point definitely, a side tube containing a small amount of water was attached between the photocell and the liquid air trap, and immersed in liquid air. Liquid air was also kept on the trap. The apparatus was then exhausted and the mercury surface brought to its normal running behavior. The line 2653A 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 about $2\frac{1}{2}$ hours. The brine was then removed and the fall was

2. Edgar Meyer, Ann.d.Phys., 65, 335, 1921.

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 due to the release of water noted. It may be argued that too much water was released. It seems probable, though, that at some point of the observations water must have been present in as small amounts as when the liquid air trap is allowed to warm. The evidence is against the theory that water vapor causes a rise in the long wavelength limit.

Since stopcocks were a necessary part of the apparatus, it is evident that vapors from the stopcock grease must be condensed in the liquid air trap, and might be responsible for the threshold of 2850A. To test this, the side tube containing water was removed, and one holding a small quantity of the stopcock grease was sealed in its place. This was immersed in liquid air, the apparatus evacuated, and the mercury surface brought to normal behavior. This required longer running than usual, indicating that the looked for impurity was present in larger quantity. When the liquid air was removed from the grease, the sensitivity rose just as it did when liquid air had been removed from the trap in the earlier experiment, the threshold reaching and holding 2850A quite exactly. The indications are, then, that some volatile component of the stopcock grease is responsible for this value of the limit. This is not conclusive, since the grease was standing for several days before the experiment of removing the liquid air was tried, and small amounts of other substances might have diffused to the tube containing it.

6. Hydrogen In Contact With The Surface.

In the latter part of Kazda's paper he tells of the effect of air, oxygen, and hydrogen

on the threshold. He found that, with a slow rate of flow of the surface, the threshold was raised by hydrogen to 2910A. His hydrogen was taken from a tank, however, and he points out that his result is not conclusive, due to the undoubted presence of impurities. It was therefore decided to test the effect of pure hydrogen.

The apparatus used in generating and purifying the hydrogen is shown in fig.7a. It was generated electrolytically from water containing a little sulphuric acid. A large jar was used to prevent undue rise in temperature. The positive electrode was placed inside a porous cup to prevent diffusion of oxygen to the other electrode. Brine at about -5°C was circulated through the jacket around the tube in which the hydrogen was generated. This reduced the pressure of water vapor to a low value. When the tube was full of hydrogen the stopcock was opened and the hydrogen admitted to the P_2O_5 tube, thence to the large bulb containing sodium at 100°C. This apparatus had of course been previously exhausted. The hot sodium should remove all traces of oxygen. All remaining impurities were then removed by allowing the hydrogen to pass through charcoal immersed in liquid air. It then passed through another liquid air trap before finally entering the photocell. The method of introducing the sodium to the bulb is shown at fig.7b. The bulb, already sealed to the rest of the apparatus, had at first the small bulb and inclined tube connected to it. The sodium was cut into small cubes, washed in absolute ether, dried, and dropped into the inclined tube. The end of this tube was then closed and the whole exhausted. The tube was then heated until the sodium melted and ran through a plug of glass wool into the small bulb. The inclined tube was sealed off and removed. The sodium was then distilled from the small bulb into the large one, and the small bulb

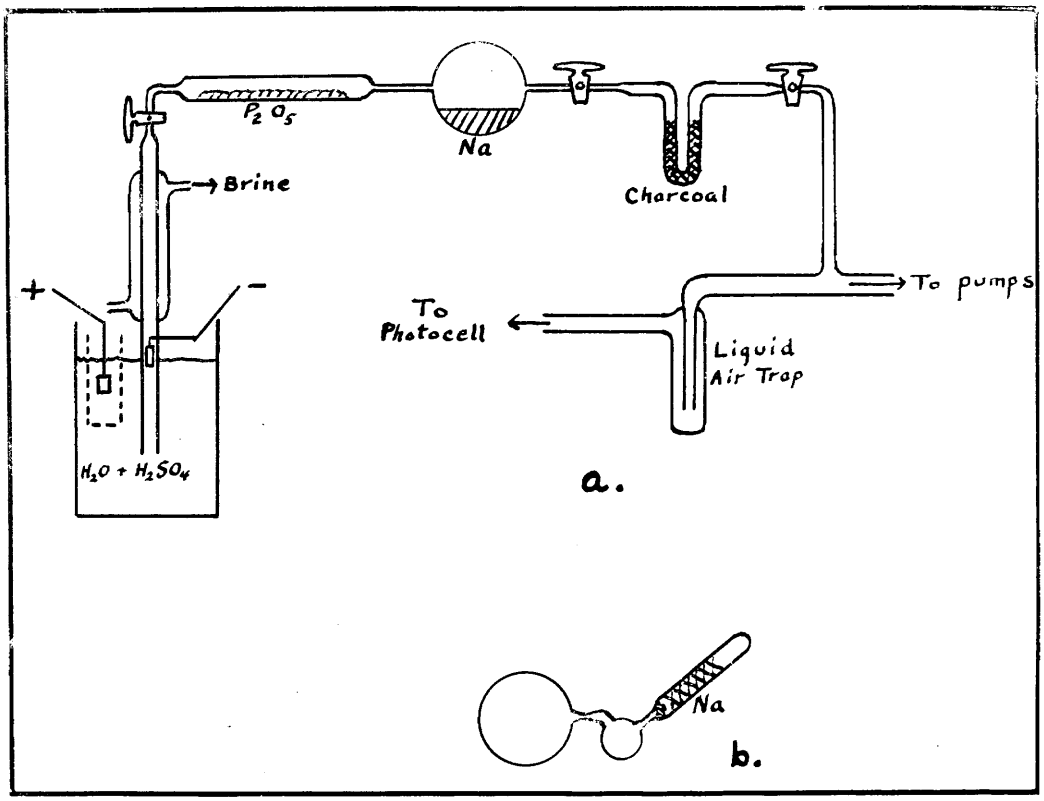

Fig. 7. Apparatus for generating and purifying hydrogen.

removed. The charcoal was activated by heating at 500° for four hours, before the hydrogen was passed through it.

The results obtained with this pure hydrogen were entirely negative. Pressures used varied from 10^{-4} mm up to .1 mm. The experiment was tried with a standing surface and with the surface flowing at various rates, including rates as low as that for which Kazda found the limit of 2910A. In all these experiments the photocurrents behaved exactly as they did in a high vacuum, except that when pressures of .001 mm or higher were used a decrease in the photocurrent resulted. This decrease was undoubtedly a space, not a surface, effect, for it was roughly proportional to the pressure, and similar pressures of air gave similar decreases. Also, the photocurrent always came back to its former value immediately on pumping out the gas, this holding whether the surface was running or standing. *In no case was any rise of sensitivity observed on admitting the hydrogen.* The still was also turned off while hydrogen was present, and the behavior was exactly as in a high vacuum (see fig.3). We must then conclude that Kazda's high limit with hydrogen was due to an impurity. It seems to be something I have not encountered in any of my work, for I have never found a threshold greater than 2850A. I have never observed a deflection with the line at 2894A that could not be fully accounted for by stray light, as determined by setting slightly off the line and getting the same deflection. Pure hydrogen, in contact with the mercury surface, does not modify the surface in any way that changes the photoelectric behavior. This conclusion is confirmed by the results of the next section.

7. 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. On the basis of this theory he explains the results of several observers on photoelectric and thermionic behavior, and on a few other effects. I have told of one result of my own that does not conform to his theory, - that of the rise of sensitivity of a running surface when liquid air is removed. This is quite evidently a case of the formation of an adsorbed film, and the effect is an increase in emission. It occurred to me that I might further test his theory by letting the mercury distill in the presence of a gas, expecting that some of the gas would be dissolved in the condensing mercury and carried through to the cell where the surface is exposed. While Suhrmann thinks that other gases may play the same role, he states that hydrogen is probably responsible for the increase in many cases. Therefore hydrogen was the logical gas to use for this test.

On an examination of fig.1, it is seen that the still is connected with the photocell only by two small tubes, both of which are full of mercury. A pressure of several cms. could be maintained in the still without altering the high vacuum in the photocell. Both parts of the apparatus are connected with the same pumps, but can be separately closed off by means of large mercury-sealed stopcocks. A separate liquid air trap is provided for each branch. The connection from the hydrogen generator led to the branch connected with the photocell. In order to introduce hydrogen to the still it was then necessary

3. Rudolf Suhrmann, Zeit.f.Tech.Phys., 4, 304, 1923.

to fill both branches with the gas, then shut off the branch connected with the still and proceed to pump out the other. The surface was first made to flow, the normal threshold, about 2740A, being exhibited (curve I, fig.9). Hydrogen was then allowed to enter at a pressure of 8 mm. of mercury, the branch to the still immediately closed off, and the other branch pumped out. As explained in section 6, the photocurrent dropped on introducing the hydrogen, falling from 103 mm (for λ=2653A) to 25 mm, but it immediately came back to its former value on pumping out. The electrometer deflection was then closely watched for more than two hours, during which time the small tube leading from still to photocell must have emptied many times. No appreciable change was observed during this time. The still was then turned off, and the sensitivity rose to a maximum of 398 mm, which is almost exactly what I had been getting with a high vacuum in both branches. There was this important difference, however, - that *the time required for the rise was 49 minutes.* Two days before, the time required for this rise had been 12 minutes. In fact, in the year preceding and the two months following the experiment described here, I observed this time of rise under high vacuum conditions some 27 times, and always found it between 11 and 20 minutes. The 20 minute rise had been observed on only one occasion, the most common value being 13 minutes. Thus it is seen that the 49 minute rise indicated a radical difference in behavior. Curve I, fig.8, shows the time of rise as taken two days before, i.e. without hydrogen present. Curve II shows the first rise obtained with hydrogen present in the still. For both curves the still was turned off at the time marked zero.

Curve I, fig.9, is the threshold curve for the running surface, both with and without hydrogen in the still. Curve II was taken after the highest sensitivity had been reached, fifty

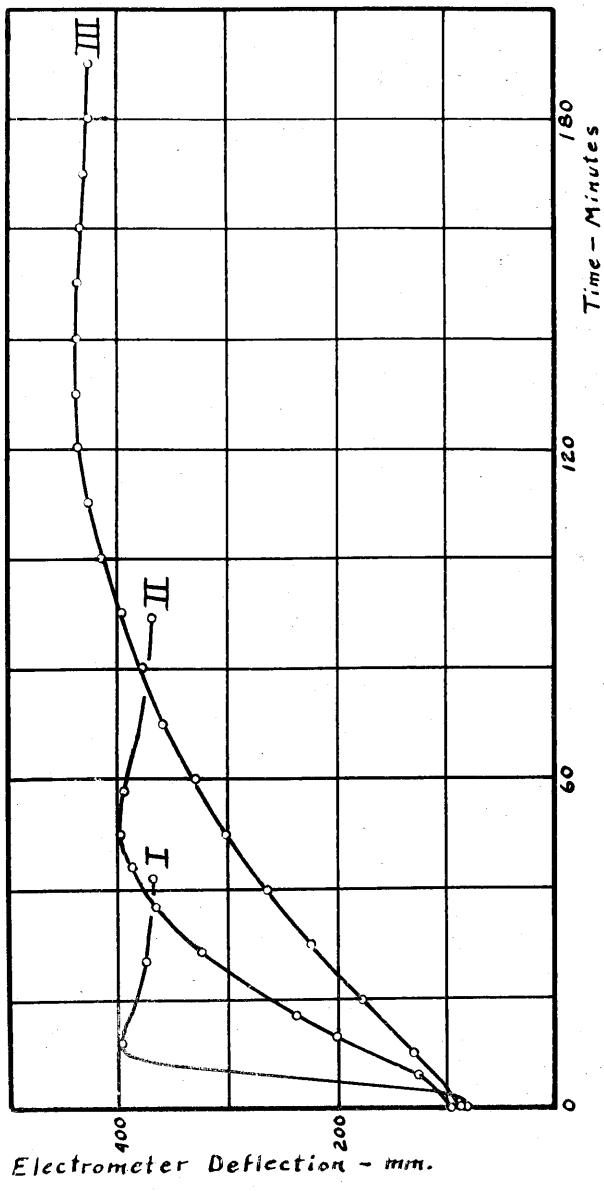

Fig. 3. Rise of sensitivity on stopping surface flow.
I, In high vacuum.
II and III, With hydrogen in the still.

minutes after turning off the still. The threshold 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.5, obtained similarly but without hydrogen present, it is seen that the rate of fall of the threshold is now much less. The whole effect of the hydrogen then seems to be a slowing of the rate at which changes take place.

After curve V of fig.9 had been taken, the still was again started. The hydrogen was allowed to remain in the still. After two hours of running the normal threshold of 2735A was obtained. The time of rise after turning off the still was 44 minutes. On the next day the normal threshold was again found for the running surface, but the time of rise on turning off the still had increased to 84 minutes. A slow fall similar to that shown in fig.9 was then observed over the next three days. When the still was then started, brought to normal behavior, and turned off again, 124 minutes was found to be necessary for the rise to maximum sensitivity. This is shown in curve III, fig.8. In all cases the threshold reached the maximum of 2850A.

The hydrogen, which had remained in the still all this while, was then pumped out. The pumping was continued for several days, the still being operated at the same time, so as 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.

It was recognized that there might be some objection due to the fact that hydrogen was admitted to the photocell, even though for a short time only. Therefore the whole experiment was repeated at a later date, the connection from

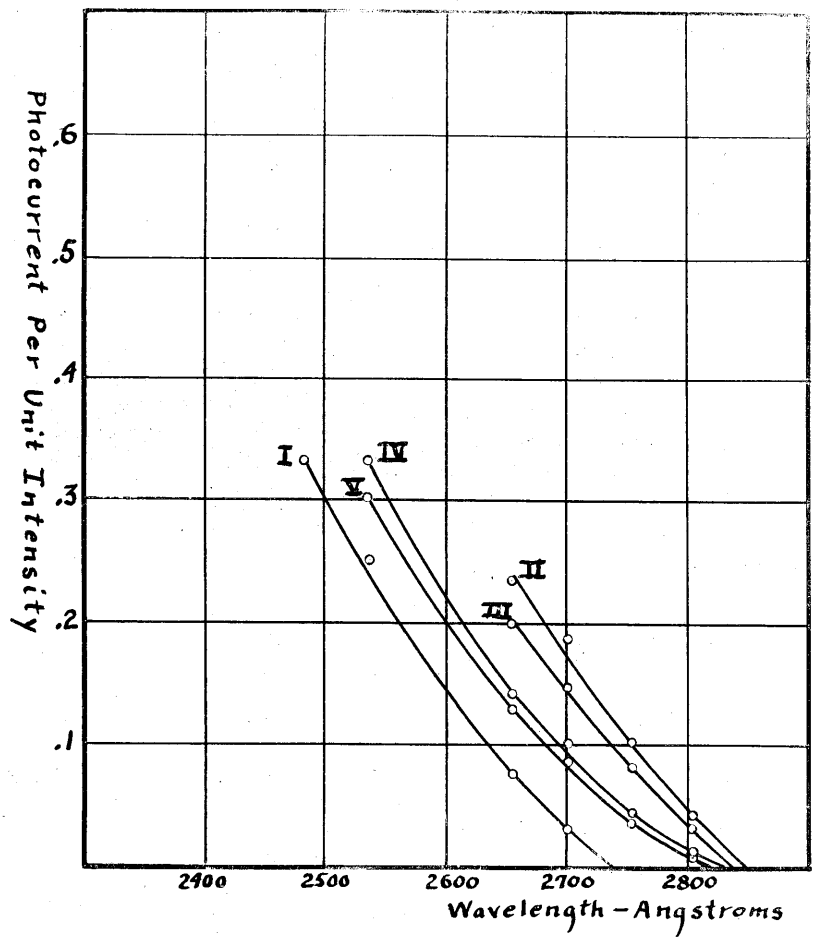

Fig. 9. Change of threshold with hydrogen in the still.

I	Curve for flowing surface.
II	50 minutes after turning off still.
III	14 hours " " " "
IV	85 " " " " "
V	110 " " " " "

the hydrogen generator being changed this time so that it led directly into the still. The day before admitting the hydrogen, the time of rise to maximum was observed to be 19 minutes. The threshold then dropped to 2675A in 19 hours. With the still running, this part of the apparatus was completely shut off from the rest and hydrogen then admitted at eight mm. pressure. The electrometer deflection was observed for two hours and no change noted. Then on turning off the still the time required to reach the maximum was 122 minutes. The value of the limit at maximum was 2850A. Then in 19 hours it fell to 2750A, and in 32 hours to 2670A. This was a more rapid fall than that shown by the curves of fig.9. Still it was not as rapid as the fall observed just before the hydrogen was admitted, while this latter was much more rapid than the fall shown by the curves of fig.5. This only means that the impurity responsible for the fall was present in the photocell in greater quantity than during the earlier experiments. This was quite possible, for the apparatus had been used in various ways in the meantime. It is seen that in all essential respects the results of this last experiment with hydrogen checked those of the former.

The important facts are these:- (1) A marked difference in the rate at which changes take place is observed when hydrogen is present in the still. These changes are in other respects already familiar to us. (2) The sensitivity and long wavelength limit of the running surface remains unchanged.

From (1) we conclude that a solution of hydrogen in the condensing mercury occurs, that the dissolved hydrogen is carried to the photocell, and that its effect is to impede the action of other impurities attacking the surface.

In view of this conclusion, (2) tells us that hydrogen dissolved in the mercury has no appreciable effect on the characteristic photoelectric behavior of the metal. This evidence is definitely against Suhrmann's theory.

It appears likely to me that the results of several other investigators might be explained by assigning to hydrogen the property of retarding or preventing the action of other impurities. For example, Tucker[4] has found that by prolonged heating at a high temperature the threshold of platinum is brought below 1850A. It then rises rapidly on cooling. Now it may be that the extreme heating completely drives out the hydrogen from the outer layers of the metal, and that this absence permits some other impurity to attack the metal, lowering the threshold. On cooling, more hydrogen may diffuse outward from the interior of the metal, driving away the impurity. Of course this is only a suggestion - I do not offer it very seriously. More reasonable would be an explanation of the results of Dumpelmann and Hein[5], who found that the photoelectric sensitivity of a metal plate is increased by the electrolytic generation of either hydrogen or oxygen on the opposite side of the plate. It seems very probable that the gas diffusing through the plate drives away some surface impurity that is holding down the sensitivity. In general, except where hydrides or other compounds are definitely known to be formed, any effect due to hydrogen may as well be an indirect effect, through its action on some other agent, as a direct action on the metal.

I wish to express my warmest thanks to Prof. R. A. Millikan for his direction in this

4. F.G.Tucker, Phys.Rev., 22, 574, 1923.
5. R.Dumpelmann and W.Hein, Zeit.f.Phys., 22, 368, 1924.

work. My thanks are also due Dr. C. B. Kazda for turning his apparatus over to me and for his help at the beginning of my work.

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