CRITICAL PHOTOELECTRIC POTENTIAL OF CLEAN MERCURY
AND THE INFLUENCE OF GASES AND OF THE
CIRCULATION OF THE MERCURY UPON IT

BY WAYNE B. HALES

Abstract

The apparatus used by Kazda and Dunn for the determination of the critical
photoelectric potential of mercury has been completely reconstructed. The stop-
cocks, the grease of which was the source of contaminating vapors, have been re-
placed by mercury cut-offs and the high temperature cement used in the construc-
tion of the photo-electric cell has been replaced by a graduated quartz-Pyrex seal. Fresh
clean mercury was returned to the still. With this new apparatus and under these new
working conditions the long wave-length limit for running mercury has been found
to be 2735Å. The conditions within the apparatus have been found to be practically
free from contaminating vapors so that the critical frequency has been found for
stationary mercury, namely 2735 ± 10Å, which is in entire agreement with Kazda for
flowing mercury. This impurity in the old apparatus caused the photo-current to in-
crease four-fold its original value in thirteen to twenty minutes after the still was
turned off. It then slowly receded, falling below its initial value in three or four
days. This increase in the photo-current was accompanied by a rise in the threshold
to 2850Å, thence falling in time to a constant value 2680Å. In the apparatus as it
now stands this same four-fold increase is not reached until some eighty hours
after the still is turned off and remains perfectly constant indefinitely thereafter.
The long wave-length limit for this maximum sensitivity was found to be 2910Å.

Hydrogen, helium, argon, nitrogen, and water vapor in extremely small quanti-
ties in contact with the surface and also, except in the case of water vapor, dissolved
in the body of the mercury, had no influence whatever upon the photoelectric behavior
of the mercury or upon the rate of rise of sensitivity upon turning off the still except
that each had a marked cleansing effect in reducing the concentration of the impurity
which slowly contaminates the surface. Oxygen had a decided reducing effect upon the
threshold value, bringing it down to 2555Å in eighteen hours.

I. Introduction

The phenomenon of photoelectric fatigue has for years been the subject
of many exhaustive experimental studies. This fatigue has been explained
in all cases as being due to either chemical, physical, or electrical modifica-
tions of the surface. In fact, Hallwachs, Wiedemann and others maintained
that it is the modified surface and not the material itself that exhibits these
photoelectric properties and if absolutely clean surfaces could be had they
would be insensitive to the action of light. The Hallwachs theory states
that photoelectrons are due to adsorbed and absorbed gases; that the ad-
sorbed layers of gas on the surface hinder the discharge of photoelectrons,
while the absorbed gas in the metal assists the process of discharge of elec-
trons. Without going farther into the discussion of these theories, it is now
generally conceded through the work of Elster and Geitel, Pohl and Pringsheim,
Millikan, and others that the photoelectric activity of a pure metal is an
intrinsic property of that metal, and that no fatigue would be observed with
a clean metallic surface in a perfect vacuum.
PHOTOELECTRIC POTENTIAL OF Hg

The greatest difficulty, therefore, in this field has been to realize these conditions. Metallic surfaces have been brought to a maximum of purity by prolonged heating at high temperatures, the surface again modifying itself slowly as it is brought back to lower temperatures. In 1923 Kazda succeeded in obtaining the most satisfactorily clean surface ever hitherto had. His measurements were made on a flowing surface of mercury which very recently had condensed from the vapor state. This surface was in contact with the contaminating impurity for only a few seconds, a time altogether too short for the contamination to become effective. He was thus able to establish accurately the critical photo-electric potential for flowing mercury at \( 2735 \pm 10 \text{A} \), and this as an intrinsic property of mercury itself. The fact that his work was done at ordinary room temperature was a distinct contribution to this field of investigation. Kazda found, however, that as soon as the mercury surface became stationary it was immediately changed either by gases\(^1\) modifying its surface or else through some molecular arrangement which was different when stationary from that when flowing. Kazda, therefore, was never quite sure but that his value of \( 2735 \text{A} \) for the critical potential of mercury was characteristic only of a moving mercury surface.

In 1924 Dunn\(^2\) began an investigation with the same apparatus to determine the cause and nature of the surface contamination. He found by using a radioactive leak that the photo-current was increased four times its initial value when the mercury surface became stationary and then slowly receded below its initial value. The threshold immediately changed from \( 2735 \text{A} \) to \( 2850 \text{A} \) thence falling in three or four days to \( 2680 \text{A} \). Stopcocks were used in Kazda’s apparatus. Among other things Dunn investigated the effect of the vapor from stop-cock grease upon the photoelectric behavior of mercury by inserting a small quantity in a lateral tube. He found that when liquid air was taken off this tube the impurity was present in the apparatus in sufficient quantity to attack the running surface regardless of how fast the surface was changing, giving this same threshold value of \( 2850 \text{A} \).

According to this then it is possible for the flowing surface to be modified. The thought, therefore, presented itself that the high temperature cement which was used in the construction of the photo-cell and which was immediately above the mercury, together with the vapors arising from\(^3\) the stop-cock grease, could also attack the running surface and that \( 2735 \text{A} \) is the threshold value for the contaminated surface.

Furthermore, the recent work of Sophie Taubes\(^3\), wherein she established \( 3043 \pm 20 \text{A} \) as the critical photoelectric potential of mercury drops suspended in a Millikan condenser, makes it desirable again to determine the threshold wave-length by Kazda’s method after every possible source of contamination has been removed. To determine the effect of these changes in the apparatus on the photo-electric behavior of mercury and to investigate the modifica-

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\(^1\) Kazda, Phys. Rev. 26, 643 (1925).
\(^2\) Dunn, Phys. Rev. 29, 693 (1927).
\(^3\) Sophie Taubes, Ann. d. Physik 76, 6, 629 (1925).
tions introduced when various gases were present in the apparatus, the present study was undertaken.

II. Apparatus

The mercury still, Faraday cage arrangement, the quartz mercury arc, the source of ultra-violet light, the Hilger monochromator, and Dolezalek electrometer for measuring photo-current were essentially the same as described in Kazda's and in Dunn's papers. On the other hand all the glass parts of the apparatus were newly constructed and carefully cleaned and the photoelectric cell completely remodeled. The iron cup, which held the mercury in the photo-cell, was held firmly in place in the old apparatus by means of a high temperature cement. This cement which could be the source of contaminating vapors was eliminated in the new apparatus, the cup being mounted on a cone of invar so shaped as to fit in the ground glass joint. A stiff spring passed from its lower end through the glass and held the cup firmly in place.

The quartz window above the Faraday cage was originally sealed to the photoelectric cell by means of high temperature cement. This was replaced by a quartz-Pyrex graduated seal. All stop-cocks were replaced by mercury cut-offs, thus eliminating practically every source of contaminating vapors. Both still and photoelectric cell were connected through liquid-air traps to two stages of condensation pumps, these being supported by a Cenco Hyvac pump. Fresh mercury, after being cleaned by filtration, washing, and distillation, was returned to the still and cell.

The relative intensities of the lines from the mercury arc were measured by means of a delicate vacuum thermopile consisting of a single couple connected to a high sensitivity galvanometer. The photo-sensitivity and threshold values were measured and plotted as described in the papers of Kazda and Dunn.

III. Diffusion of Hydrogen Through Mercury

Much time was spent in the study of the diffusion of hydrogen through the mercury and observing the effects produced upon the photoelectric behavior of mercury. This was done with the old arrangement of the apparatus which was admirably adapted for such a study. Dunn found that hydrogen present in small quantities in the cell had no observable effect upon either the threshold of the flowing mercury or the rate of rise of sensitivity upon turning off the still and allowing the surface to become stationary. However, when hydrogen was admitted only into the still and the mercury was allowed to condense for two hours in an atmosphere of hydrogen, striking evidence was furnished that hydrogen had entered into solution with the mercury and passed over into the cell where it modified the action of the contaminating impurity upon the surface of mercury. This was revealed in the fact that the maximum sensitivity of the surface was reached in 120 minutes after the still was turned off, whereas without hydrogen present this surface condition was reached in fifteen minutes. The rate at which the sen-
sitivity receded was much less with hydrogen present than without. The maximum threshold of 2850A was found to be the same in both cases.

Dunn's experiments on hydrogen were further extended by observing whether hydrogen could diffuse from the still through the mercury to the cell when the still was not running. Another run was made in which the hydrogen was not admitted into the still until 22 minutes after the still was turned off and the mercury became perfectly quiet. The results are plotted in C of Fig. 1, curve B being the normal effect in vacuum.

It will be noticed that for the first 24 hours the curves are identical. During the next 24 hours the hydrogen has succeeded in diffusing through the mercury and has changed the photoelectric sensitivity. The corresponding effect upon the threshold was observed.

These experiments were repeated and showed identically the same effect. They furnish very striking evidence that hydrogen will diffuse through such a small tube filled with mercury, the presence of it being detected by the change in the photoelectric behavior of the mercury. The column of mercury in this case was 30 cm long and 5 mm in diameter.

IV. COMPARISON OF THE CRITICAL POTENTIAL FOR FLOWING AND STATIONARY MERCURY

After the data discussed in section III were taken the whole apparatus was rebuilt as mentioned in section II.
The results now obtained are given in Figs. 2, 3, 4, and 5. All curve showing the change of photoelectric sensitivity with the time were taken with the line \( \lambda 2653 \) A. After the mercury was placed in the still the pumps and still were operated during the day-time for four days before a reading was taken. The first set of readings is plotted in Fig. 2A. The photo-current is seen to increase four times its initial value in 6 hours and then remain constant for the next 34 hours. Curve B shows the change after four more days of pumping during which time the still was run intermittently for periods of 2 to 4 hours. Curve C is the same after 16 days pumping and reveals the same four-fold increase in photocurrent in 60 hours, remaining constant thereafter. Curve D shows the rate of rise after pumping for two months during which time the apparatus was washed several times by helium, argon and hydrogen, these gases being introduced into the apparatus for the purpose of a study to be discussed in section V. *It will be noted in D that the apparatus is so free from contaminating vapors that the surface remains practically constant for 24 hours after the mercury surface becomes stationary.*

During the course of this experiment a leak developed and it became necessary again to change the mercury in the still. After prolonged pumping the data plotted in Fig. 2E were taken and observed for 398 hours. *During all the time after it had reached a steady value the electrometer deflection did not vary more than \( \pm 20 \) mm from 390 mm.* Curve F of Fig. 2 is a characteristic curve always obtained with the old apparatus and is given here for comparison purposes only.

Fig. 3B is a curve obtained from the old apparatus showing the changes produced in the photo-current when the mercury surface which had been stationary for three or four days was broken up by turning on the still. In twenty minutes the condensation of mercury in the still begins to break up the con-
taminated surface. The photo-current immediately rises to a maximum value and in about three hours returns to its normal value. During its return to normal the photo-current fluctuates by as much as 25 mm. This is shown by the scattered nature of the points through which curve B of Fig. 3 is drawn.

Curve A of Fig. 3, is the same phenomenon observed with the reconstructed apparatus. It will be noticed that these fluctuations are entirely absent, that all the points lie on the curve, and that the photo-current reaches its normal value in one hour after the still is turned on as compared with three hours for the old apparatus. This is added evidence that the contaminating vapors are present in very much less quantity than formerly.

Fig. 4 contains some threshold curves made with the new apparatus. Curves A and B represent runs made on flowing mercury locating the critical photo-electric potential at 2735 ± 10A, exactly the same as found by Kazda and Dunn. Curve C was taken at the time of maximum sensitivity during the early stages of pumping. This gave a threshold of 2910A. This was always a reproducible value when air was admitted to the apparatus two or three times in immediate succession. Since this maximum sensitivity was maintained for so short a time in the old apparatus Dunn was never able to make a successful determination of the maximum threshold in the usual way. His constant value of 2850A could reasonably have been 2910A. In fact, this 2910A value was observed by Kazda in his measurements with hydrogen in the cell. However, in the apparatus as it now stands after prolonged pumping the threshold for maximum sensitivity becomes constant at 2850A as shown by curves D and G. Curve E was obtained when the clean mercury surface had been exposed to dry air at atmospheric pressure for thirty minutes. This air was admitted through four long drying tubes containing CaCl₂ and P₂O₅. Curve F is the same as for E except that the air was left in contact with the mercury over night. The long wave-length limit for a mercury surface thus modified by dry air is quite definitely placed at 2555A units. This fact will be referred to in section V. The curves in Fig. 5 were taken at the same time as the data for curve D, Fig. 2. Curve A, Fig. 5, gives the threshold of 2732A for the flowing surface. Curve B gives the value 2743A for the surface which has been stationary for 21 hours. Curve C gives the value 2755A for the surface standing 46 hours and curve D gives the value 2770A for the surface standing in vacuum 70 hours. A threshold run taken 10 hours after the surface became stationary did not show any change in this critical frequency. These curves were taken after two months of pumping and washing with inert gases. They reveal, together with Fig. 2D that the apparatus is practically free from contaminating vapors, thus
affording an excellent opportunity to study the effect of different gases in modifying the photoelectric behavior and in changing this critical photoelectric potential.

Discussion of results. These data taken in high vacuum permit the following conclusions to be drawn:

First. The critical photoelectric potential for flowing mercury has been found to be the same in the new and old apparatus. This means that the impurities in the old apparatus were not present in sufficient quantities to change its threshold value. This also more firmly fixes 2735 Å as the long wave-length limit for clean mercury since it was done with new mercury and under new working conditions and constitutes an independent check of Kazda's work.

Second. The impurity was present in sufficient concentration in the old apparatus to make it uncertain whether the threshold of 2735 Å was unique to a turbulent flowing surface and whether the same threshold would obtain for an absolute quiet surface. Threshold values determined two hours and, later, ten hours after the surface became stationary, showed no change whatever in the critical frequency. It can be stated with certainty, therefore, that the critical photoelectric potential for moving mercury is identical with that for stationary mercury and that this value is 2735 ± 10 Å.

Third. The impurity in the old apparatus which caused the rapid rise of photo-current to four times its initial value in 20 minutes is now greatly reduced in concentration as this same four-fold increase in sensitivity is not reached until about 80 hours after the still is turned off. This maximum value has been observed to remain constant for 398 hours.

Fourth. Dunn did not know whether the following decrease in sensitivity was due to further increase in the deposit of but one impurity or whether it was due to the action of a second impurity which acted very much slower than the first. These experiments with the new apparatus clearly show that it must have been a second impurity, probably coming from the high temperature cement, which is entirely absent in the new apparatus. During six months of observation not a single instance was ever noted when this sensitivity ever decreased. One case was observed for 398 hours without any decrease occurring.

Fifth. Two theories are given to explain the increase in sensitivity. First: A layer of molecules of the impurity is slowly adsorbed on the surface of mercury, the presence of which facilitates the release of the photoelectrons from the surface, thus increasing its sensitivity. When a monomolecular layer completely covers the mercury surface it has lost its power to adsorb more and the photo-current remains constant and after prolonged pumping the surface settles to a long wave-length limit of 2850 Å. Second: When molecules of the impurity are adsorbed by the mercury, a surface of the impurity is gradually substituted for the mercury surface and what is then measured is the photoelectric behavior of the impurity and not that of the mercury.
V. Effect of Gases on this Stationary Critical Potential

The gases studied were hydrogen, helium, argon, water vapor, nitrogen, and oxygen. They were introduced into the apparatus in the above mentioned order. Each gas-generating apparatus could be attached without permitting air to enter either the cell or still compartments. The apparatus was always thoroughly pumped out, the pumps operating for three or four days, before successive gases were admitted.

Hydrogen. The hydrogen was generated electrolytically, the water vapor being taken out by circulating brine and $\text{P}_2\text{O}_5$. Traces of oxygen were eliminated by holding the gas in an atmosphere of sodium vapor at 110°C for three or four hours. The hydrogen, as well as all other gases except water vapor, was then passed through an activated charcoal trap collé to liquid-air temperature. The hydrogen, when in the cell or dissolved in the mercury in the still, did not change the photoelectric behavior of the mercury. Even when hydrogen of 3 cm pressure was in contact with the surface for 48 hours and then pumped off, no apparent changes from the normal effects were seen. Curves $A$ and $B$, Fig. 6, show the effect of hydrogen when dissolved in the mercury, $A$ being the normal effect, $B$ the hydrogen effect. There is not sufficient difference to attribute any real effect to the hydrogen. Comparing this with similar curves obtained by Dunn we see a marked difference. The effect in curve $B$, Fig. 6, would be expected to be more normal since the impurity upon which hydrogen manifests itself is practically absent from the apparatus.

Helium. Helium was taken from a drum of the Texas source and was purified by circulating it through a trap held at 500°C. The trap contained copper shavings, which removed the oxygen, magnesium ribbon, which removed the nitrogen, and copper oxide, which removed the hydrogen. After passing over $\text{P}_2\text{O}_5$ and through activated charcoal at liquid-air temperature it was sufficiently pure for the purpose of the experiment. Observations taken when helium was present in the cell only and when dissolved in the mercury showed no change from normal behavior, either upon the surface sensitivity or upon the critical potential.

Argon. Argon taken from a flask furnished by the General Electric Company was introduced into the apparatus and showed the same lack of effect. No change was observed in the rate of rise of sensitivity or upon the critical

![Fig. 6. Change of photo-sensitivity: $A$, normal effect in vacuum; $B$, effect of hydrogen dissolved in mercury; $C$ and $D$, effect of water vapor released from 95 percent H$_2$SO$_4$ solution at $-20^\circ\text{C}$ and at $20^\circ\text{C}$.](image)
frequency because of the presence of these three gases, namely, hydrogen, helium, and argon. The only effects these three gases had was that of washing the impurity out of the apparatus and thus reducing the rate of rise of photo-electric sensitivity.

Water vapor. Water vapor was introduced into the apparatus early in the experiment by joining a lateral tube between the photo-cell and the liquid-air trap. The tube containing the water vapor was separated from the apparatus by a mercury cut-off so that vapor could be held and released at will. To reduce the concentration of water vapor five drops of distilled water were dissolved in ninety-five drops of concentrated sulphuric acid. An approximation from available tables shows that the vapor pressure for such a mixture is not larger than 0.01 mm at ordinary temperature or 0.001 mm at \(-20^\circ\)C, the temperature of a salt and ice mixture. The effect of the water vapor on the photo-current is shown in curves C and D, Fig. 6.

For the first forty hours the sulphuric acid-water mixture was held at \(-20^\circ\)C by means of a salt and ice mixture. The behavior during this time was quite normal. At this time the cooling mixture was taken off and the sensitivity thereafter fell. The threshold, however, remained constant at 2785 A, and is shown in curve B of Fig. 7. Curve D of Fig. 6 was taken for water vapor freed from the solution at ordinary room temperature where the pressure of water could be from 0.01 to 0.05 mm. The rate of rise is seen to be very much slower. The threshold for this case after 20 hours was found to be 2800 A, and remained constant for the next 50 hours. This is given in curve C, Fig. 7. It is safe to conclude, therefore, that 2800 A is the critical potential characteristic of mercury in the presence of small quantities of water vapor. Kazda's statement that extremely small quantities of water vapor had a marked effect upon stationary mercury and raised its long wavelength limit, has not been checked in this experiment, but rather the conclusion is drawn that extremely small quantities of water vapor do not materially change the photoelectric behavior of mercury. Furthermore, this is concurrent with conclusions drawn by Richardson\(^4\) for the action of water vapor upon a potassium surface.

Nitrogen. Nitrogen was prepared by removing the oxygen from the air by slowly sucking air through six wash bottles, the first four containing copper trimmings and equal amounts of concentrated ammonium hydroxide and concentrated ammonium chloride solution. The fourth bottle showed no coloration indicating that all the oxygen had been removed. The last two wash bottles contained concentrated solutions of sulphuric acid and removed all traces of water vapor.

At the time nitrogen was introduced the apparatus had been pumped out for two months and was practically free from contaminating vapors. The method used to determine the effect of nitrogen was to stop the still and observe the change in critical frequency after 24 hours; first, when the surface stood in vacuum and, second, when it had stood in 10 cm of nitrogen.

The effect in both cases gave this critical frequency as 2750A. After the surface had stood for 91 hours in the presence of 10 cm pressure of nitrogen the long wave-length limit had risen to 2800A. This threshold determination is shown graphically in curve D, Fig. 7.

It is concluded that mercury is insensitive to the action of nitrogen in this molecular form.

Oxygen. The oxygen was prepared by heating potassium permanganate to 400°C. The oxygen liberated was passed through a plug of glass wool, thence over P₂O₅, and then through activated charcoal held at liquid air temperature. When quantities of oxygen of less than 0.005 mm pressure were added to the cell no effect was noted on the threshold for the running mercury surface. When the still was turned off and the surface became stationary, 5 cm of oxygen was admitted to the cell and still. After 18 hours this was pumped off and a threshold determination made. It is represented in curve E, Fig. 7, giving a threshold of 2555A. Five cm of oxygen was again placed in the still and cell without disturbing this surface. After another 52 hours the oxygen was pumped off and a threshold run made. This is represented in curve F, Fig. 7, giving a threshold value of 2560A. If these two curves are compared with curves E and F of Fig. 4, which resulted when dry air was in contact with the stationary mercury surface, we find exactly the same critical frequency appearing. We can conclude, therefore, that the only element in dry air which attacks the mercury surface is the oxygen and the critical frequency thus determined is for a mercury oxide film. This value was checked on a second determination similar to the above. The critical photoelectric potential for a mercury surface in contact with pure oxygen can be placed at 2555 ± A.

Stop-cock grease. While no special attempt was made to determine the effect of stop-cock grease upon the photoelectric behavior of mercury by introducing it specifically into the apparatus, it is evident that it plays a very important part. In fact the only way the rate of rise in sensitivity could be increased was by letting air into the apparatus through a stop-cock. This air would carry with it small quantities of grease vapor and thereby increase the concentration of the contaminating impurity.

VI. Summary

The results of this investigation may be summarized as follows:

First. Hydrogen will diffuse through a column of mercury 30 cm long and 5 mm in diameter from the still to the cell in a time between 24 and
48 hours and modify the action of contaminating vapors in the photoelectric cell.

Second. The changes in the construction of the photo-cell and apparatus have (a), eliminated entirely the impurity which attacked the stationary mercury surface and reduced its sensitivity; (b), practically eliminated the impurity which attacked the stationary mercury surface and increased its sensitivity; (c), resulted in conditions within the photo-cell so free from impurity that the surface remained practically constant for hours; (d), permitted the determination of the critical photoelectric potential for a clean stationary surface of mercury. Its value was found to be $2735 \pm 10\,\text{A}$, agreeing completely with the value found by Kazda for flowing mercury.

Third. Hydrogen, helium, argon, and nitrogen have no effect whatever upon the photoelectric behavior of either moving or stationary mercury. The surface is modified the same when in the presence of these gases as when in a high vacuum. Water vapor at very low pressure has no effect; at higher pressures it acts as an inhibiting agent to the action of other slight traces of impurity which attack the stationary mercury surface. Oxygen and dry air have a marked effect on the photoelectric properties and reduce the critical potential to $2555\,\text{A}$ in a short time.

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Norman Bridge Laboratory of Physics
California Institute of Technology
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