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

A Thesis

Presented to the Faculty of

The California Institute of Technology

in Partial Fulfillment of the

Requirements for the

Degree of Doctor of Philosophy

DEPARTMENT OF PHYSICS

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MAY 1926

CONTENTS

The apparatus used by Kazda and Dunn for the determination of the critical photo electric potential of mercury has been completely reconstructed. The stop cocks, the grease of which was the source of contaminating vapors, have been replaced by mercury cut offs and the high temperature cement used in the construction of the photo cell has been replaced by a graduated quartz-pyrex seal.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 2735A°. 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± 10A°, which is in entire agreement with Kazda for flowing mercury.

This impurity in the old apparatus caused the photo current to increase 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 raise in the threshold to 2850A°, hence falling in time to a constant value 2680A°. 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 2910A°.

The effect of hydrogen, helium and argon in contact with the surface and dissolved in the body of the mercury was found to have no influence whatever upon the photo electric 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.

Nitrogen in contact with the surface was found to have no effect except that the maximum threshold reached when nitrogen was present was 2800A°. Water vapor at very low pressure inhibits the action of the sensitizing impurity and gives a threshold of 2800A° after being in contact with the surface for seventy hours. Oxygen has a decided reducing effect upon the threshold value, bringing it down to 2555A°

in eighteen hours. Another fifty-two hours exposure to oxygen does not materially change this value. Air, at atmospheric pressure, in contact with the surface gave this same threshold value, namely, 2555A°.

II. INTRODUCTION

The phenomenon of photo electric 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 modifications of the surface. In fact, Hallwacks, Weideman, and others maintain that it is the modified surface and not the material itself that exhibits these photo electric properties and if absolutely clean surfaces could be had they would be insensitive to the action of light. The Hallwacks theory states that photo electrons are due to adsorbed and absorbed gases; the adsorbed layers of gas on the surface hindering the discharge of photo electrons, while the absorbed gas in the metal assist the process of discharge of electrons. Without going farther into the discussion of these theories, it is now generally conceded through the work of Pohl and Pringsheim, Millikan, Elster and Geital, and others that the photo electric activity of a pure metal is an intrinsic property of that metal, and that no fatigue would be observed with a clean metalic surface in a perfect vacuum free from all vapors which may contaminate the surface.

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 Dr. C. B. Kazda[1], working in the Norman Bridge Laboratory, succeeded in obtaining the most satisfactorily clean surface hitherto ever had. His measurements were made on a flowing surface of mercury which very recently was 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±10A°, and this as an intrinsic property of mercury itself. His work being done at ordinary room temperatures 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 modifying its surface or else through some molecular arrangement which was different when stationary

1. Kazda, Phys. Review, Vol. 26, p. 643, Nov. 1925

than when flowing. Kazda, therefore, was never quite sure but that his value of 2735A° for the critical potential of mercury was characteristic only of a moving mercury surface.

In 1924 Dr. Hugh K. Dunn[1], began an investigation with this apparatus to determine the cause and nature of this surface contamination. He found by using a radio active 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 2735A° to 2850A° hence falling in three or four days to 2680A°. He investigated the effect of water vapor, hydrogen, and stop cock grease upon the photo electric behavior of mercury. The latter becomes of interest at this point. Since stop cocks were a necessary part of the apparatus it was important to know what/the individual effect of stop cock grease would be. Dunn, therefore, inserted a small quantity of this in a lateral tube on the cell side of the liquid air trap. He found that when liquid air

1. Dunn, Doctor's Thesis, Calif. Inst. of Tech., 1925.

was taken off this lateral 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 four fold increase in photo current and this same threshold value of 2850A°.

According to this then it is possible for the flowing surface to be modified. The thought, therefore, presents 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 the stop cock grease, could also attack the running surface yielding 2735A° as a threshold value. It was, therefore, thought desirable to reconstruct the whole apparatus and eliminate these possible sources of impurity.

Furthermore, in view of the recent work of Sophie Taubes[1] wherein she established 3043± 20A° as the critical photo electric potential of mercury drops suspended in a Millikan condenser, such a

1. Ann. d. Physik, 76. 6, p. 629, April, 1925.

change would be highly desirable. With fresh mercury returned to the still results then obtained could be considered an independent check of Kazda's value. To determine the effect of these changes in the apparatus on the photo electric behavior of mercury and to investigate the modifications introduced when various gases were present in the apparatus, the present study was undertaken.

III. APPARATUS

The apparatus used in this investigation was essentially the same as that used by Kazda and Dunn. It is shown in diagram form in figure I and will be described again here. The still consisted of an ordinary mercury diffusion pump. The mercury vapor was condensed by means of water circulating through the provided water jacket and fell into a tube below, hence it passed through a small glass tube over into a shallow iron cup about 2 cm. in diameter in the photo cell. When the cup contained a given amount of mercury it overflowed and passed back into the still to be evaporated again. The rate of discharge of mercury from the cup depends upon the rate of evaporation of the mercury from the still which in turn depends upon the rate at which current is applied to the heater. This rate could be varied at will by means of an attached rheostat. The iron cup in the old apparatus was held firmly in place by means of high temperature cement. The cement was eliminated in the newly constructed apparatus. The cup was mounted

on a cone of invar so shaped as to fit in the ground glass joint. Invar was chosen since its coefficient of temperature expansion is practically identical with pyrex glass. A stiff spring passed from its lower end through the glass and held the cup firmly in place.

Immediately above the cup and insulated from it is superposed a Faraday cage made of oxidized copper. A small slit in the top of this cage permits the ultra violet light from the illuminator condensed by a lens to fall upon the mercury. The cage receives the electrons ejected from the mercury and conducts them through a well shielded wire to the electrometer. The mercury is maintained at three volts negative potential, three volts being sufficient to maintain saturation. The quartz window above the Faraday cage was originally sealed to the photo cell by means of high temperature cement. This was replaced by a quartz-pyrex graduated seal as is indicated in figure I. The cell and the mercury leads to and from the still are covered on their outside by tin foil to prevent induced electrical charges due to the movement of the mercury from producing eradic changes in the

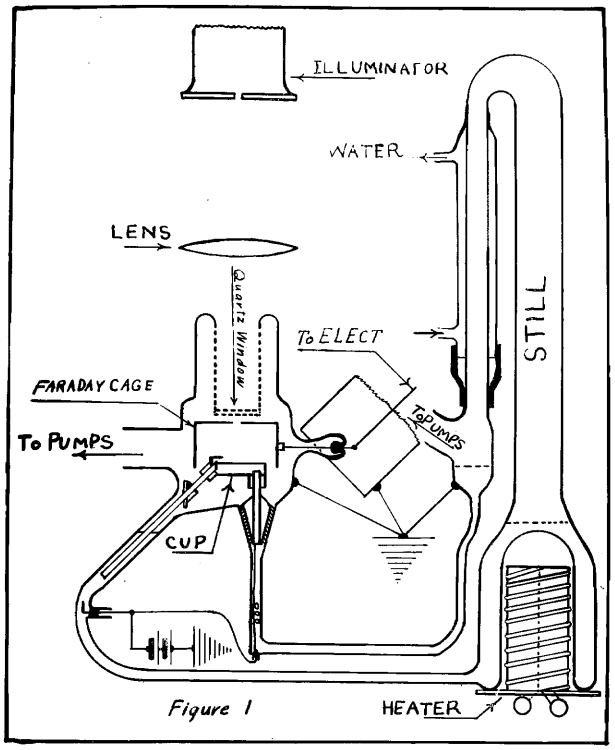
ILLUMINATOR
WATER
LENS
Quartz Window
To ELECT
STILL
FARADAY CAGE
To PUMPS
To PUMPS
CUP
HEATER

Figure 1

electrometer readings. Both still and photo cell are connected through liquid air traps to two stages of Langmuir condensation pumps, these being supported by a Cenco Hyvac pump.

The mercury used in the experiment was first filtered through chamois and allowed to fall in a fine spray through solutions of potassium hydroxide and nitric acid and washed in distilled water. This was repeated a number of times. After this wet treatment and after being dried by heating, the mercury was distilled a number of times at a low pressure and at 125° C, the residue each time being eliminated from the stock supply. Air slowly bubbled through the mercury during this process of distillation. After this treatment the mercury should be as pure as it is possible to obtain it and should be free from any impurity of sufficient amount to modify its photo electric behavior. Particular care was taken to thoroughly clean every piece of glass that went into the apparatus. After it was assembled the whole apparatus was evacuated and heated several times to drive off occluded gases before the mercury was placed in the still.

The source of light was a quartz mercury arc, mounted in an asbestos lined box. The light passed through a camera shutter hence through a Hilger monochromator, from which it passed through a quartz lens and is focused upon the slit in the Faraday cage from which it falls vertically upon the mercury surface without touching the copper oxide cage. 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 deflection of the galvanometer was observed through a telescope on a scale twenty-five feet distant. The light from the monochromator was first focused on one junction of the thermopile for maximum deflection and then focused on the other junction for maximum deflection in the opposite direction. The average of ten observations on the difference of these two readings gave a measure of the relative intensities of the lines used. The results are compiled in the following table. (Table I on next page)

Table I

Line in angstroms.	Deflection in mm. or relative intensity
2967	284
2925	66
2894	115
2803	168
2754	58
2700	71
2653	331
2537	524
2483	113
2400	50
2378	39
2345	30
2302	29

It will be noticed that these relative intensities are somewhat different than those in the lamp used by Kazda and Dunn. This should be expected as a characteristic of any mercury arc. This arc was always held at a constant voltage between 92 and 94 volts with 1.9 amperes flowing through, thus insuring constant intensities.

The needle of the Dolazalek electrometer used in measuring the photo currents was kept at a constant voltage of 138 volts. The sinsitivity measured on a scale of 150 cm. distant was held between 1040 and 1060 mm. per volt. To obtain a given threshold value the monochromator was set to transit a given line, the ground to the electrometer quadrant was removed, the shutter then opened for an interval of 8, 16, 24, etc. seconds depending upon the intensity of the light. At the end of one minute after the shutter is opened the needle has settled to a steady deflection. This deflection plus the leak which is measured during the next minute constitutes the deflection D. As 8 seconds is arbitrarily chosen as the unit of time each D is divided by 1, 2, 3, etc. to give (d) deflection per unit time. (d) is then divided by I, the intensity of the line, to give d, the photo current per unit time per unit intensity. d is then plotted against λ giving a sharp intercept on the wave length axis. This intercept is taken as the long wave length limit or critical photo electric potential. These threshold values could be duplicated at will on the constant

surface. The uncertainty could never be greater than ± 10A°. A sample table is given here.

Table II

λ	D	t	(d)	I	d
2653	109	40	21.8	331	.066
2700	13	48	2.2	71	.031
2537	148	8	148	524	.282
2483	142	24	47.3	113	.418

Giving λ_0 = 2735A°.

The constant deflection method of measuring photo currents adapted by Dunn by connecting a radioactive leak to the electrometer furnished a convenient method of observing the variation of photo sensitivity with time. This method was used throughout these experiments. It will be found described in detail in Dunn's thesis, page 6.

IV. DIFFUSION OF HYDROGEN THROUGH MERCURY

Most of the summer of 1925 was spent in a study of the diffusion of hydrogen through the mercury and observing the effects produced upon the photo electric 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 allówed 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. These experiments of Dunn were repeated with the same results and are given in curves A and B, figure 2. B represents normal rate of rise

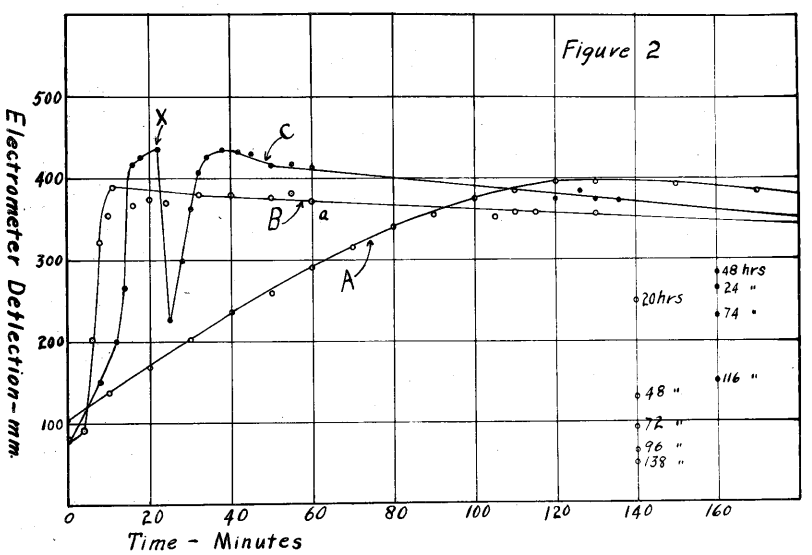
Figure 2
Electrometer Deflection - mm.
500
400
300
200
100
0
20
40
60
80
100
120
140
160
Time - Minutes
X
C
B
a
A
48 hrs
24 "
74 "
116 "
20 hrs
48 "
72 "
96 "
138 "

of photo current in vacuum when the still is turned off. A represents the rate of rise when hydrogen is in solution. In this case the maximum sensitivity is reached in 120 minutes instead of 15 minutes as in B. The rate at which the sensitivity receded was also much less in A than in B. 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 figure 2. At the time marked X, 1 cm. pressure of hydrogen was admitted to the still. The sudden fall of photo current was due to the breaking up of the surface already formed. It immediately rose to its former value. The effect upon the change of photo current with the time is more clearly represented in figure 3 where B and C are again plotted. It will be noticed that for the first 24 hours the

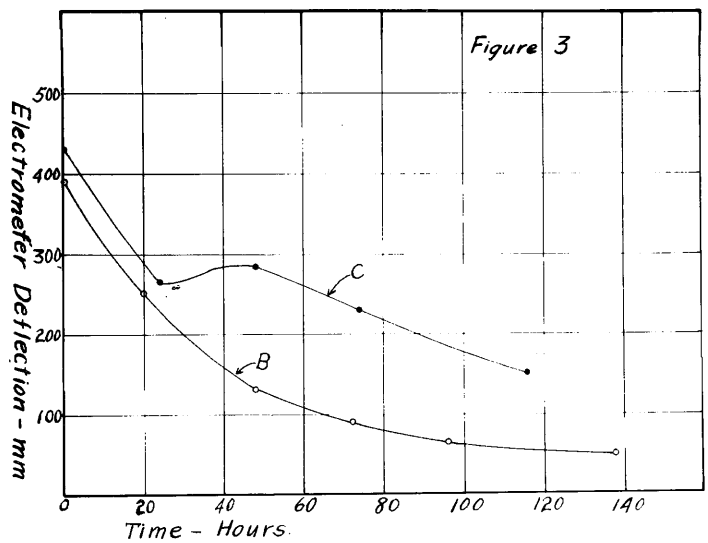
Figure 3
Electrometer Deflection - mm
500
400
300
200
100
0
20
40
60
80
100
120
140
Time - Hours
C
B

curves are identical. During the next 24 hours the hydrogen has succeeded in diffusing through the mercury and changing the photo electric sensitivity. The corresponding effect upon the threshold is given in Table no. 3.

Table III

Normal effect in vacuum		Effect with H_2 in still	
Time	Threshold	Time	Threshold
23 hrs.	2830	24 hrs.	2820
48 ''	2782	48 ''	2840
72 ''	2750	74 ''	2820
96 ''	2722	116 '''	2785
138 ''	2700		

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 photo electric behavior of the mercury. The column of mercury in this case was 30 cm. long and 5 mm. in diameter.

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

After the data discussed in section IV were taken the whole apparatus was rebuilt of new materials, the stop cocks in the old apparatus were replaced by six mercury cut offs, and the cell was redesigned to eliminate the high temperature cement which was used to hold the mercury cup in place and to seal the quartz window to the cell. A helical spring and a quartz-pyrex graduated seal replaced this high temperature cement. Fresh clean mercury was returned to the still. The only stop cock left in the apparatus which could possibly furnish contaminating vapors was on the high pressure side of the mercury diffusion pumps. Whenever air was admitted to the apparatus it had to come through this stop cock.

The results now obtained are given in figures 4, 5, 6, and 7. All curves showing the change of photo electric sensitivity with the time were taken with the line $\lambda = 2653A^{\circ}$. 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 figure 4A. 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 photo current 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 VI. 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 to again change the mercury in the still. After prolonged pumping curve given in figure 4 E was taken and observed for 398 hours. DURING ALL THE TIME AFTER IT HAD REACHED A

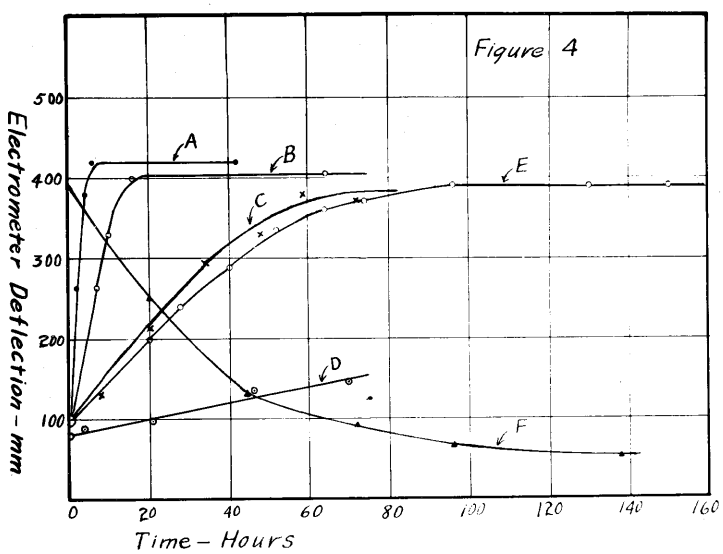
Figure 4
Electrometer Deflection - mm
500
400
300
200
100
A
B
C
D
E
F
0
20
40
60
80
100
120
140
160
Time - Hours

STEADY VALUE THE ELECTROMETER DEFLECTION DID NOT VARY MORE THAN ± 20 mm. FROM 390 mm.

Curve F of figure IV is a characteristic curve always obtained with the old apparatus and is given here for comparison purposes only.

Figure 5B is a curve similar to figure IV in Dunn's thesis. The surface of mercury has been stationary for three or four days when the still is turned on . In 20 minutes the condensation of mercury in the still begins to break up the contaminated 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 figure 5 is drawn.

Curve A of figure 5 is the same phemonenon 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

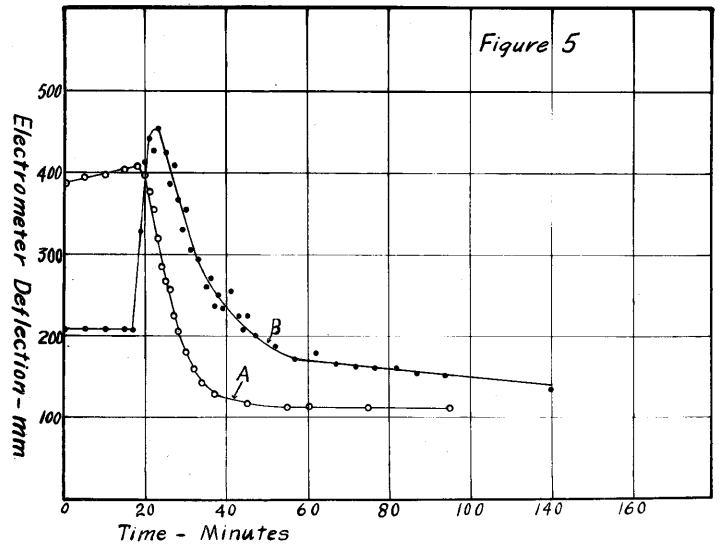
Figure 5
Electrometer Deflection - mm
500
400
300
200
100
0
20
40
60
80
100
140
160
Time - Minutes
A
B

hours for the old apparatus. This is added evidence that the contaminating vapors are present in very much less quantity than formerly . Figure VI 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 reproducable 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.

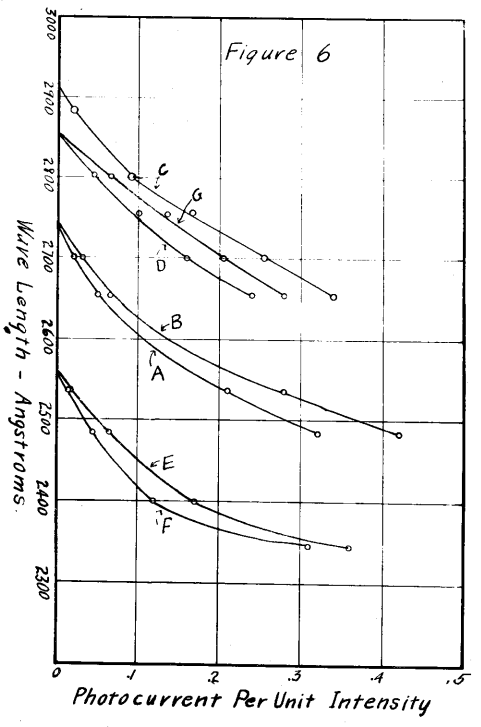
Figure 6
3000
2900
2800
2700
2600
2500
2400
2300
Wave Length - Angstroms
C
G
D
B
A
E
F
0
.1
.2
.3
.4
.5
Photocurrent Per Unit Intensity

Curve E was obtained when the clean mercury surface had been exposed to dry air at atmospheric pressure for 30 minutes. This air was admitted through four long drying tubes containing $CaCl_2$ and P_2O_5. 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 VI. The curves in figure 7 were taken at the same time as the data for curve D, figure 4. Curve A gives the threshold of 2732A° for the flowing surface. Curve B gives the value 2743A°for the surface which been stationary for 21 hours. Curve C gives the value 2755A° for the surface standing 46 hours and curve D gives the value 2770 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 figure 4D that the apparatus is practically free from contam-

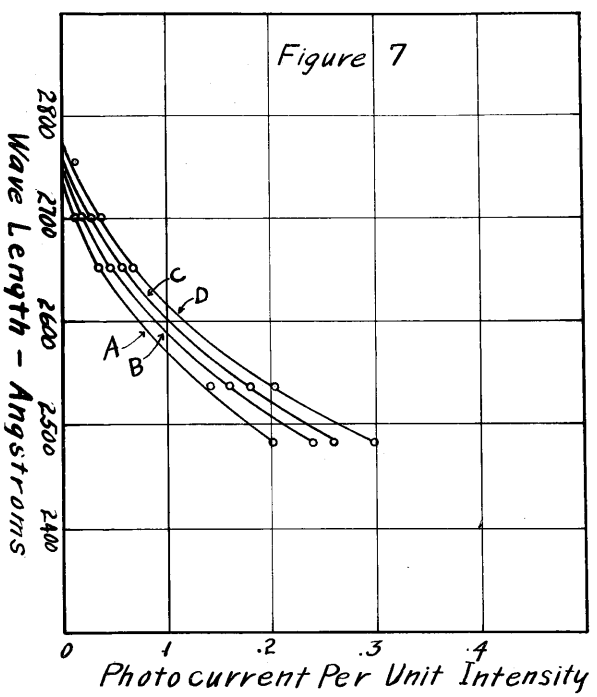
Figure 7
2800
2700
2600
2500
2400
Wave Length - Angstroms
A
B
C
D
0
.1
.2
.3
.4
Photocurrent Per Unit Intensity

inating vapors thus affording an excellent opportunity to study the effect of different gases in modifying the photo electric behavior and changing this critical photo electric potential.

DISCUSSION OF THESE RESULTS

This data taken in high vacuum have permitted the following conclusions to be drawn:-

First,- The critical photo electric 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 2735A° 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 to Kazda's work.

Second,- The impurity was present in sufficient concentration in the old apparatus to make it uncertain whether the threshold of 2735A° 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 PHOTO ELECTRIC POTENTIAL FOR MOVING MERCURY IS IDENTICAL TO THAT FOR STATIONARY MERCURY AND THAT THIS VALUE IS 2735 ±10A°.

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 occuring.

Fifth,- The increase in sensitivity is due to one of two theories. 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 photo electrons from the surface, thus increasing its sensitivity. When a unimolecular 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 2850A°. 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 photo electric behavior of the impurity and not that of the mercury.

VI. 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 P_2O_5. Traces of oxygen were eliminated by holding the gas in an atmosphere of metallic 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 cooled to liquid air temperature. The hydrogen, when in the cell or dissolved in the mercury in the still did not change the photo electric

behavior of the mercury a particle. Even when 3 cm. were left 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, figure 8, 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 curves A and B of figure 2 we see a noted difference. The effect in curve B, figure 8, would be expected to be more normal since the impurity upon which the hydrogen manifests itself is practically absent from the apparatus.

HELIUM - Helium was taken from a drum of the Texas source purified by circulating it through a trap held at 500° C containing copper shavings, which removed the oxygen; magnesium ribbon, which removed the nitrogen;and copper oxide, which removed the hydrogen. After passing over P_2O_5 and through activated charcoal at liquid air temperature it was sufficiently pure for the purpose of the experiment. Figure 9 gives the result of measurements on helium. Curve A gives the normal

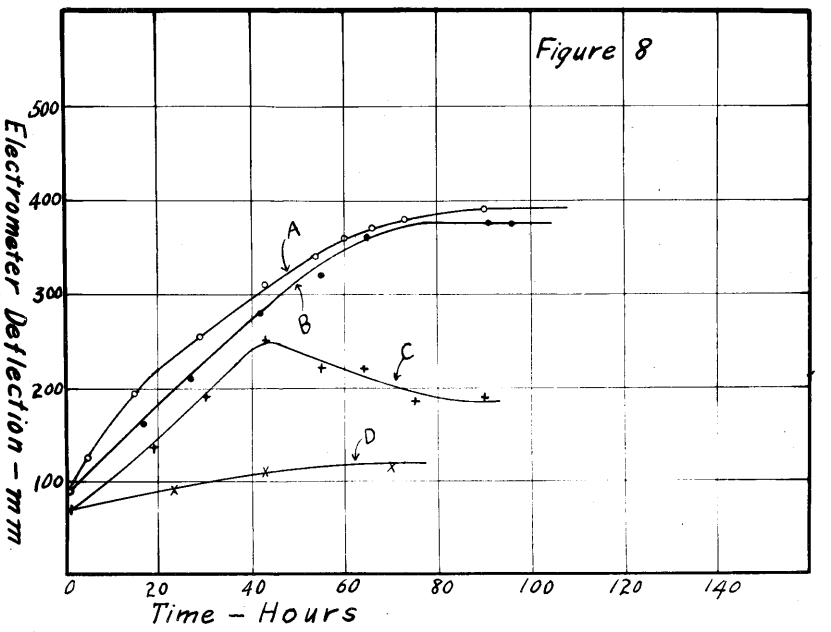
Figure 8
Electrometer Deflection - mm
500
400
300
200
100
0
20
40
60
80
100
120
140
Time - Hours
A
B
C
D

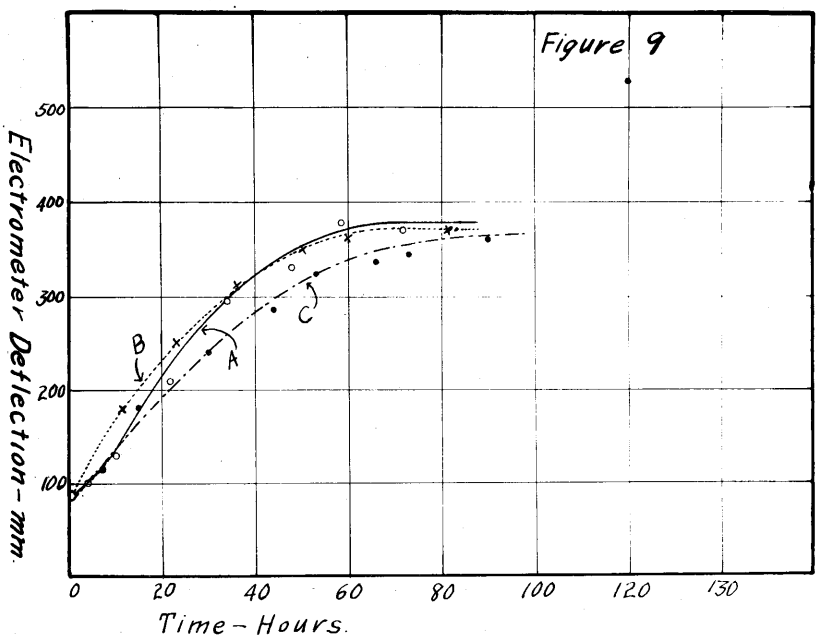
Figure 9
Electrometer Deflection - mm.
500
400
300
200
100
0
20
40
60
80
100
120
130
Time - Hours.
A
B
C

rate of rise of photo electric sensitivity in vacuum. Curve B gives the effect when .005 mm. pressure of helium was present in the cell only. Curve C gives the effect when 1 cm. pressure of helium is present only in the still and the mercury condenses in its presence for 2 hours.

Argon taken from a flask furnished by the General Electric Company was introduced into the apparatus and showed identically the same inactive effects. No change was observed on the rate of rise nor upon the critical frequency by the presence of these three gases, namely, hydrogen, helium, and argon. The only effect 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 means of a

mercury cut off so that vapor could be held and released at will. To reduce the concentration of water vapor 5 drops of distilled water were dissolved in 95 drops of concentrated sulphuric acid. An approximation from available tables shows that the vapor pressure for such a mixture could not be larger than .01 mm. at ordinary temperature or .001 mm. at -20° 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, figure 8.

For the first 40 hours the sulphuric acid, water mixture was held at -20° C by means of a salt and ice mixture. The behavior during this time is quite normal. At this time the cooling mixture was taken off and the sensitivity thereafter falls. The threshold, however, remained constant at 2785A°, and is shown in curve B of figure 10. Curve D of figure 8 was taken for water vapor freed from the solution at ordinary room temperatures where the pressure of water could be from .01 to .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 2800A°, and

remained constant for the next 50 hours. This is given in curve C, figure 10. It is safe to conclude, therefore, that 2800A° is the critical potential characteristic for mercury in the presence of small quantities of water vapor. Kazda's statement in his paper[1] that extremely small quantities of water vapor had a marked effect upon stationary mercury and raised its long wave length limit, has not been checked in this experiment, but rather a conclusion is drawn that extremely small quantities of water vapor do not materially change the photo electric behavior of mercury. Furthermore, this is concurrent with conclusions drawn by Richardson, for the action of water vapor upon a potassium surface. The effect of large quantities of water vapor as tested in Dunn's work (see his thesis) was not studied in the present apparatus.

NITROGEN - Nitrogen was prepared by removing the oxygen from the air by slowly sucking air through six wash bottles, the first four containing cop-

1. Proc. Royal Soc., vol. 107, p. 387.

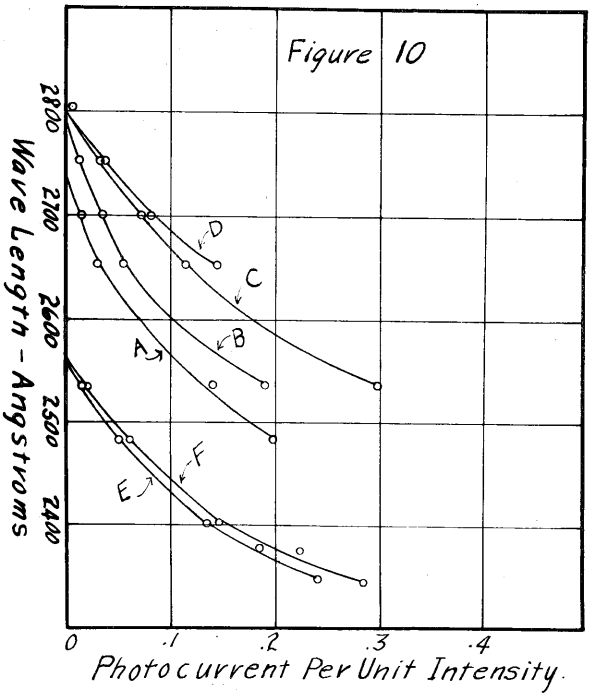
Figure 10
2800
2700
2600
2500
2400
Wave Length - Angstroms
D
C
B
A
E
F
0
.1
.2
.3
.4
Photocurrent Per Unit Intensity.

per trimmings and equal amounts of concentrated ammonium hydroxide and concentrated ammonium chloride solution. The 4th 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 2800. This threshold determination is shown graphically in curve D, figure 10.

The conclusion is drawn 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, hence over P_2O_5, then through activated charcoal held at liquid air temperature. When quantities of oxygen of less than .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, figure 10, giving a threshold of 2555A°. 5 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, figure 10, giving a threshold value of 2560A°. If these two curves are compared with curves E and F of figure 6, 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 photo electric potential for a mercury surface in contact with pure oxygen can be placed at 2555 $\pm$10A°.

STOP COCK GREASE - While no special attempt was made to determine the effect of stop cock grease upon the photo electric 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 that the rate of rise in sensitivity could be increased was by letting air into the apparatus through the stop cock mentioned. This air would carry with it small quantities of grease vapor and thereby increase the concentration of the contaminating impurity.

VII. 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 cm. 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 photo electric 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 whcih 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 photo electric potential for a clean stationary surface of mercury. Its value was found to be 2735 $\pm$ 10A°, agreeing completely with the value found by Kazda for flowing mercury.

Third, - Hydrogen, helium, argon, and nitrogen have absolutely no effect upon the photo electric properties of either moving or stationary mercury. The surface is modified the same when in the presence of these gases as when in high vacuum. Water vapor at very low pressure has no effect, at higher pressure 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 photo electric properties and reduce the critical potential to 2555A° in a short time.

In conclusion the author wishes to express his appreciation to Dr. Robert A. Millikan for setting him to work on this problem, and for the helpful suggestions given during the progress of the experiment. Grateful recognition is given to Dr. Hugh K. Dunn for acquainting him with the experimental technique of the problem. He also wishes to thank Mr. Pearson and Mr. Clancy for the willing service rendered in the construction of the apparatus.