ENERGY CONTENT OF MERCURY ARC LINES
AND THE
PHOTOELECTRIC EFFECT FOR MERCURY

Thesis

by

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Abstract

A. - Energy Content of ultra-violet lines of the quartz Mercury Arc.

By means of a vacuum thermocouple it is possible to use a Leeds and Northrup high sensitivity galvanometer for these measurements directly. The sensitivity of the couple is increased from 6 to 15 fold by operation in a vacuum. Stabilization of the operation of the arc enables one to get accurate and reproducible results for long periods of time. The deviation from average between 3000A and 2400A does not exceed 2.2%. Limitations due to absorption by quartz and air and also to the increasing amount of stray light below 2400A causes the deviation to increase up to 10% at 2225A.

B. - Long Wave-Length Limit of a clean surface of liquid mercury.

Apparatus is designed to permit continual distillation and intermittent overflow of the mercury in the same circuit. Rate of change of surface can be varied. For a wide range of rapidly changing surfaces the long wave length limit is found to be constant and independent of the presence of gases in the photochamber. The long wave-length limit of Mercury is fixed at 2735A and is an intrinsic property of the metal. The maximum deviation, from average, of the photocurrents is 2.8% down to 2300A for successive measurements.

C. - Influence of Dry Air, Oxygen and Hydrogen on the Long Wave-length limit and photocurrent.

When the surface is slowed up or allowed to become stationary gases affect it. Hydrogen very quickly raises the limit to a new value and increases the photocurrents considerably. Oxygen very slowly lowers the limit and decreases the photocurrents. The behavior of air is attributed to the hydrogen and oxygen it contains. It is concluded that pure metals do have a definite photo-effect and that the effect is modified by the presence of gases either occluded or in the neighborhood of the metal and that gaseous conditions may be stable enough to give reproducible effects which vary depending on the elements entering into the combination.

D. - Discussion.

A brief summary of previous methods used in photoelectric work and recent theoretical explanations are given. The simultaneous measurement of photocurrents and presentation of clean surface is a distinct advantage.

A list of references is put at the end.

INTRODUCTION

Following the early phase of discovery by Hertz[1], Hallwachs[2], Lenard[3] and J. J. Thomson[4], later experimentation in the field of photoelectricity has been uncertain because of the apparently conflicting evidence presented by different investigators. No attempt will be made here to enumerate these various investigations for that has been done by others in many reports and may be found in the literature on the subject.

It may be well, however, to state that these later investigations may be divided into two groups. To the first belong those of Friedenhagen[5], Wiedemann and Hallwachs[6], Kustner[7], Hughes[8], Sende and Simon[9], Suhrmann[10], and others[11]. The results of their experiments and the conclusions they drew from them would throw serious doubt upon the existence of the phenomenon as an intrinsic property of the material under investigation. They conclude that the presence of impurities is an essential condition for the phenomenon to exhibit itself. In the second group we have the investigations of Pohl and Pringsheim[12], Piersol[11], Millikan and his students[13], Welo[14], Elster and Geitel[15], and others[11]. They obtained sizeable photocurrents in all cases. They experimented with variation of total photocurrent mainly.

Some of the investigators, (Koppius[16], Tucker[17], and others), worked on the shift of the photoelectric threshold. They found that the threshold could be shifted. In some cases the threshold value was shifted beyond the limits of their apparatus to determine.

The explanation advanced by the first group is that the effect is one between the metal and a surface film of reacting gas, and when this reacting gas is carefully removed the effect disappears. I was able to produce conditions which would give the same results as theirs, but which were not contradictory to the validity of previous experimentation on the photoelectric effect. The main factors involved in the differences between the above two groups of experiments have to do with the treatment of the material studied and the conditions under which the experiment is carried out. Unfortunately, the detailed description of experiments as reported in the literature are very meagre and often not given or the description of the experimental part is mixed up with the theoretical part. If one were completely informed on each experiment reported, it would be quite possible to attribute some of the contradictory evidence to methods of procedure. I mention this because I have been able to change the conditions of my experiment so as to reproduce results, reported in both of the above mentioned groups of experiments. Of course, one main objection to the earlier experiments is that the ability to produce and maintain a high vacuum was limited and we may safely rule out many of the experiments on the basis of that fact. Even with the degree of vacuum obtainable today, there are still many molecules per c. c. left and distillation in the presence of these molecules may easily cause a change in the character of the surface which while not visible to the eye certainly is experimentally shown.

The early work of Elster and Geitel[15], over a short range and later that of Lenard[3], (and J. J. Thomson[4] independently), over a wide range, were the fore-runners of the application of the quantum theory to the photoeffect. They showed that a proportionality existed between the photocurrent and the intensity of the incident light. In 1905, Einstein[18] made the first direct application of the quantum theory to the photoeffect. He suggested the following well known equation:-

$$\tfrac{1}{2} mv^2 = Ve = h\nu - V_0 e$$

The validity of this equation has been established throughout the range of visible, ultra-violet and X-ray frequencies. The evaluation of "h" by Millikan[19] in his photoelectric experiments affords the most accurate value yet obtained. The direct implication of this equation is that each material has a photoelectric threshold characteristic of the material itself. In other words, it suggests that the threshold frequency is an intrinsic property of the material. This being the case, it is quite important to establish beyond doubt the validity of the photoelectric threshold and to devise an experiment which will be free from the possible objections to previous experiments.

Therefore, it was decided to use mercury as the material to be tested. It could be readily distilled and handled so as to be freshly presented to the incident light and subjected to a variety of tests in order to repeat the conditions of previous investigators and to go one step further, viz:- to be able to establish the photoelectric long wave-length limit of mercury as an intrinsic property of the material and independent of the presence of reacting gas in the photochamber.

To determine the long wave-length limit, the photocurrents per unit intensity were plotted against the wave lengths used. The intercept on the wave length axis gave the limiting wave length. This is identical with the method given by Millikan[19]. Thus it was necessary to investigate carefully, the method of measuring the intensity of the incident light; the measurement of the photocurrent and the determination of the long wave-length limit; and also the flexibility of the apparatus for use in the varying conditions of test as regards influence of gases inthe chamber, etc. Therefore, the report will be divided along those lines.

A. - Accurate Measurement of the Energy Content of Extreme Ultra-Violet Lines of the Quartz Mercury Arc.

Experimental Description

The accuracy of the determination of the long wave-length limit of a substance is dependent, in part, upon the accuracy of the determination of the intensity of the lines used. In this investigation the source was a Cooper-Hewitt quarts mercury arc, 100-125 volts d. c., enclosed in an asbestos lined box. The light emerged from the box through a hole about $1\frac{1}{2}$ inches in diameter and then entered the monochromatic illuminator. From the monochromatic illuminator the light, by means of a double convex lens, was concentrated upon a thermopile which was supported inside of a chamber that could be evacuated.

In order to get sufficiently sensitive apparatus for intensity measurements previous experimenters have used thermopiles in air with Paschen or Thomson Galvanometers to measure the thermoelectric currents produced by the lines. One of the most accurate measurements previously made was that of Koppius [16]. Anyone who has had occasion to use magnetically shielded galvanometers will agree that they are a mighty tedious proposition and require painstaking care to set up and operate. Even then they show a fluctuation of as much as 10% and only average readings are taken. In order to get around this difficulty use was made of the type of vacuum thermocouple employed by Pettit and Nicholson [20] at the Mount Wilson observatory and a high sensitivity d'Arsonval galvanometer.

The sensitivity of the magnetically shielded galvanometers for uses of this kind is about 10^{-10} amperes. The sensitivity of low resistance, high sensitivity Leeds and Northrup, galvanometers is about 10^{-9} amperes. Since the operation of the thermopile in a vacuum increases its sensitivity from 6 to 15 fold, one can get around the use of magnetically shielded galvanometers for this kind of work. It should be mentioned here that the behavior of thermocouples presumably made in the same way from the same stock of materials is not uniform. During this investigation a number of couples were made. Some showed drift very badly and were discarded, others showed no drift at all and remained useful for long periods of time, reproducing results which checked very well.

There seems to be no definite reason why about every other couple from the same batch should show drift while the others did not. It cannot be due to a great many factors since the chance of getting a drift free couple is so good. However, the couples used behaved consistently until mechanically broken. These couples were made of bismuth and bismuth plus 5% tin. The receiver was made of tin blackened on the receiving side and placed at the junction. The couples were of the compensated type and the double deflection was used, eliminating the zero reading. The detailed description of the construction and behavior of these couples will be omitted here, since it can best be obtained by referring to the article of Pettit and Nicholson [20]. All of the couples used were made by Dr. Pettit at the Mount Wilson observatory. The photograph shown in figure 1 was taken through the quartz window of the thermopile chamber and is magnified about three times.

Figure 1.

It will be noted that the thermopile consisted of four couples connected in parallel. This was the last couple used and gave exceedingly good results with a high sensitivity since its resistance was nearly equal to that of the galvanometer.

It is mounted upon the two platinum leads which are sealed into a glass plug. Using sealing wax, a glass plate is mounted below and a fine glass tube, to support the center of the thermopile, is fixed upon it. Directly below the couples, on the glass plate, is placed a piece of fluorescing paper. In this case use was made of a portion of the same kind of paper which comes with fluoroscopes, as it gave the best results over longer periods of use.

The light coming from the monochromatic illuminator was focused by a lens on the thermopile junctions. A special carriage was made for the lens which permitted, by a fine screw adjustment, the movement laterally from one row of junctions to the other and also by another screw adjustment permitted the movement up and down for focal adjustment. By the use of both of these screw motions, a maximum reading was always obtained for each line and this accounts for the very good agreement of the individual readings obtained.

To insure constancy of operation of the mercury lamp while readings were being taken, it was necessary, in the beginning, to make a careful study of the operating conditions of the lamp. In the preliminary tests, it was operated with the auxiliary resistance which comes with it. A test was made at various voltages and currents in order to find the values of voltage and current for which the voltage and current varied least and to observe the change in intensity as measured by the thermopile for these values. It was found that a variation of 3 % in the voltage while the current was constant was easily detected by the thermopile. In order to further reduce this variation, a resistance and reactance were connected in series with the lamp, and 200 volts from a storage battery source was used. A further test of the best operating conditions revealed that for this lamp, when operated at 92 to 93 volts and 2.1 amperes, it was possible to hold the voltage to within one volt. A large Weston direct reading standard volt meter was connected across the lamp terminals. An ordinary voltmeter measured the total voltage and an ammeter measured the current used. The standard voltmeter across the lamp terminals

had a long needle and variations of a volt were easily detectable. During intensity measurements the readings of voltmeters and ammeter were constantly noted. A variation of one volt could not be detected in the intensity measurements by the thermopile. It might be mentioned here that it took about one hour and a half for the lamp to reach these best conditions of operation after starting up.

Another important factor was to operate the thermopile under least varying conditions. If reference is made to the article of Pettit and Nicholson[20], it will be seen that the sensitivity curve is almost level beyond 10^{-4} mm.Hg. pressure. The thermopile chamber in our tests was directly connected to a two stage mercury diffusion pump and that to a Cenco hyvac pump. A liquid air trap just beyond the thermopile cell was always used when the thermopile was in operation. The pressure in the cell, as measured by the McLeod gauge, was always better than 10^{-5} mm.Hg. The cell was surrounded by cotton to insure uniform temperature on all sides.

The thermoelectric current was measured by a Leeds and Northrup, high sensitivity d'Arsonval galvanometer. It was found necessary to suspend it by a Carman[21] suspension. Its resistance was $10\frac{1}{2}$ Ohms and its sensitivity of the order of 10^{-9} amperes. In our case, the scale was about 25 feet from the mirror of the galvanometer and after reflection from the galvanometer mirror was read by a telescope about three feet from the mirror. The smallest divisions on the scale were millimeters. The only advantage gained by putting the scale off at that distance was that it was unnecessary to estimate the reading to fractions of a millimeter as it would have to be done if the scale were at the usual distance. If a sufficiently fine crosshair were put into the telescope it would have been possible to take readings to fractions of a millimeter, but this was found unnecessary for our purpose.

Results

The slit width used in all measurements of intensity was twenty divisions.

This corresponds to 0.5 mm. Tucker[17] made a measurement of the intensity for the same lines, but used a slit width of 25 divisions. He also made a photographic test which showed that the lines indicated by the drum were the only ones transmitted in this region with the exception of 2650A. The stray light which always accompanies this type of optical system and which appears as a general background on photographic plates gave a measurable thermopile deflection, but no definite conclusions regarding the nature of this stray light is proposed. The stray light readings represent the minimum reading between the lines and they clearly show that as we get down to 2300A and lower, its effect becomes so large as to almost mask out the lines themselves. This has been noted before by Souder[22]. Not all of the column headed "between the lines" can be considered due to stray light, since in some cases the minimum between the lines was not as prominent as at other places, because there are weak lines there. For this reason only the lines marked * are taken as stray light readings. In the absence of any definite reason for assigning stray values to different portions of the spectrum used, the nearest stray light value to the lines measured was used. The method is limited by this fact as well as by the fact that at 1900A, we begin to get strong absorption by air and quartz.

Table I gives a representative set of readings in mm. and indicates how close the individual readings are. It will be noticed that down to 2400A the ~~present~~ percent deviation from average is less than 2% in nearly all cases, but in other measurements, not here given, the agreement was even better. This set was the only one for which consistent readings were obtained for 2200A. One couple gave measurable deflections for 2000A consistently.

TABLE I

Wave-lengths in A.		Readings in mm.				Average	Max % Deviation from Average	Stray	Corrected Average
Lines	Between Lines	1	2	3	4				
	*3000	13	13	13		13			
2967		218	214	220		217	1.3	13	204
2925		55	53	54		54	1.8	13	41
2894		86	87	88		87	1.2	14	73
	*2840	14	14	14	14	14			
2804		142	144	146	144	144	1.4	14	130
2754		43	45	44	44	44	2.2	22	22
	*2726	22	23	21	22	22			
2700		53	52	53	53	53	1.9	22	31
2653		274	274	277	280	277	1.1	21	256
	2620	43	44	43	44	43			
2537		370	369	368	367	369	0.6	19	350
	*2505	19	19	20	20	19			
2483		90	93	91	93	92	2.1	16	76
	*2435	11	15	13	13	13			
2400		31	33	31	31	31	1.9	13	18
2378		28	30	30	30	29	3.3	15	14
	*2360	15	15	13	16	15			
2345		21	22	21	20	21	4.5	14	7
	*2330	12	14	12	15	14			
2302		17	20	17	20	19	8.1	10	9
	*2275	9	11	10	10	10			
2253		13	14	13	15	14	7.1	10	4
2225		10	11	10	9	10	10.0	6	4
	*2200	6	5	6	7	6	16.7		

Table II gives the average values of the deflections for three sets of readings in mm. This table is given only for the region of wave-lengths used in parts B and C of this report. These sets of readings are taken under the same experimental conditions, the voltage across the lamp being 92 to 93 volts and the current 2.1 amperes. The lamp could have been run at higher temperatures to get greater intensity but the precautions that would have to be taken were not warranted since sufficiently large readings were obtained for this region of wave lengths.

Table II

Wave-lengths in A.	A. 9 - 3 - 23		B. 9 - 12 - 23		C. 9 - 15 - 23		Average of Uncorrected Av.	Ratio to 2537
	Correct Av.	Uncorr. Av.	Correct Av.	Uncorr. Av.	Correct Av.	Uncorr. Av.		
2804	133	146	130	144	130	147	146	4.0
2754	37	54	22	44	23	49	49	1.3
2700	49	66	33	54	34	60	60	1.6
2653	272	289	255	276	260	283	283	7.8
2537	332	350	350	369	348	368	362	10.0
2483	81	96	76	92	81	97	95	2.6

While the readings do change from time to time, it has been found that, over the intervals of time used in the latter part of the investigation, the readings remained constant. Readings taken one set after another, during the same afternoon, do not change hardly at all. The average of the above uncorrected readings compare very well with those of Tucker[17] for relative intensities. However, this is merely a coincidence.

B. Precise Determination of The photoelectric Long Wave-Length Limit of a Clean Surface of Liquid Mercury.

Experimental Description

Extreme care was taken to obtain pure mercury, completely remove the occluded gases from it and to measure the photocurrent as soon as the fresh surface is presented to the vacuum chamber. In this way two important objections to previous experiments are removed, namely, complete removal of occluded gases and the immediate measurement of photocurrents.

Mercury was purified by the method given by Hewlett and Minchin[23] and is the same as that used by Harkins[24] in preparing mercury for use in isotope determinations. The method consists in evaporating mercury while bubbling air through it. To further insure its purity, the wet process[23] was first employed. The mercury is then put into a specially designed distillation apparatus provided with a means for bubbling air through it. This distilling process was repeated several times. The first distillate had a very slight oxide film on it, while the last two had none. After passing through pinholes in a filter paper funnel, it was ready for use.

The mercury cleaned as above mentioned was placed into a still directly connected with the photoelectric chamber. This still was made of pyrex glass shaped like one stage of an ordinary diffusion pump, as shown in the diagrammatic sketch (FIG. 2) of the apparatus. The still was provided with an electric heater whereby the current could be varied by external resistance in order to vary the rate of evaporation. Mercury is evaporated and condensed in the presence of mercury vapor again and again. The process is carried on at low pressures since the still is directly connected to the vacuum pumps. It should be mentioned that all of the apparatus was carefully cleaned, washed and dried and then heated for some time while being evacuated before mercury was finally inserted.

Preliminary experiments were necessary before the method of presenting the mercury to the illumination were worked out. A reference to the sketch shows that the mercury cup was specially constructed. The mercury flow is intermittent and the outlet is at the surface of the liquid and inclined at a 45 degree angle. The reason for this inclination will be evident later. In order to ascertain that this intermittent flow would clean the surface, rough experiments with mercury and a glass cup with a "v" groove in it were carried out. Through a strong magnifying glass, (and later a

microscope) after a few overflowings, even the trace of oil which had been dropped on the surface could not be distinguished. Fine dust could be observed to be drawn out through the groove from all parts of the surface. Continuous overflow was also tried, but it was observed that the center of the surface remained stationary, while the mercury flowed out at the groove from underneath. Thus the intermittent flow was a definite means for the removal of surface films which might possibly form when the surface is exposed to the chamber. The quantity of mercury between the condensation chamber of the still and the cup in the photochamber was small. With an intermittent flow of one gram of mercury per second, not more than a minute elapsed between condensation and overflow in the cup. From the overflow the mercury returned to the still and was re-evaporated again. In fact the amount of mercury in the still was about 125 cubic centimeters so that at the rate of overflow at the cup of one gram per second, (which was the maximum without producing continuous flow), it took only about thirty minutes for a molecule of mercury to make a complete cycle. The cup itself was very shallow so that it was covered by only a small layer at the end of each overflow. A given molecule of mercury could not remain at the surface exposed to the vacuum chamber more than a second and on the average much less than that.

The vacuum pumps were directly connected to the photochamber and run continually during the experiment. The pressure was read by a McLeod gauge and was never more than 10^{-5} mm. Hg. This does not measure the pressure of the mercury vapor which was of the order of 10^{-3} mm. Hg. at room temperature. As mentioned before the glassware was thoroughly cleaned and heated before the experiments began. A liquid air trap was situated a short distance from the photochamber. Air was never introduced except through a number of drying tubes of calcium chloride and phosphorous pentoxide.

As shown in the diagram, the cup is surrounded by a copper oxide receiver. A slit in the top permits the illumination to reach the mercury in the cup. The slit is of such dimensions as not to be touched by the concentrated light from the illuminator. The same condensing lens was used as in the intensity measurements. The thermopile chamber and the photochamber were side by side and the lateral screw motion on the holder of the condensing lens was large enough to serve both chambers.

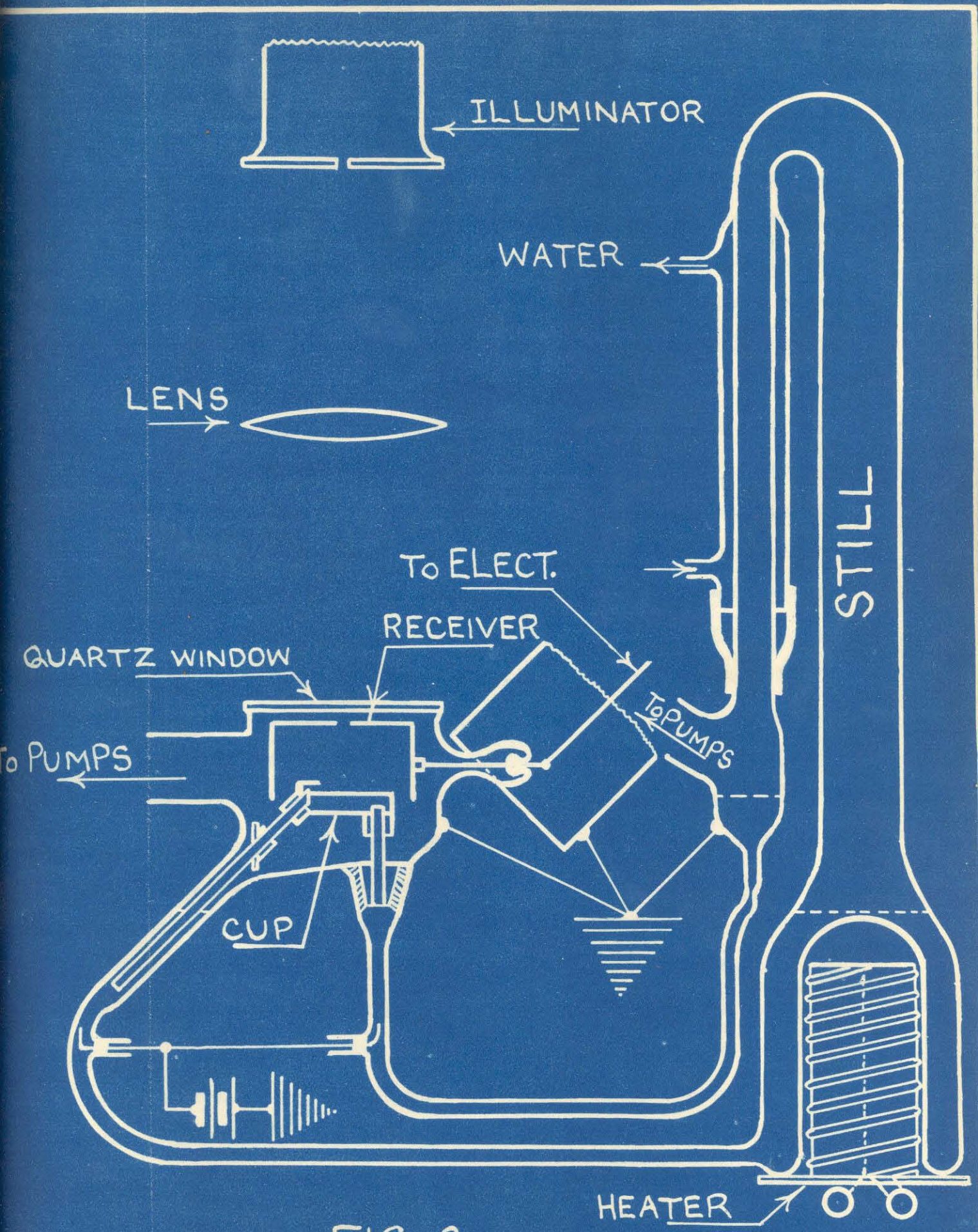

ILLUMINATOR
WATER
LENS
STILL
To ELECT.
RECEIVER
QUARTZ WINDOW
To PUMPS
To PUMPS
CUP
HEATER

FIG. 2.

The monochromatic illuminator was mounted so that both collimator and telescope were in the vertical plane after having been carefully adjusted so that the drum readings were correct. The lamp was mounted on a special carriage and rigidly connected to the illuminator, so that motion along a square guide, to which the carriage could be clamped, was possible when shifting from one chamber to the other. This moving element being heavy was counterweighted from the ceiling so that ease was experienced in making this shift quickly. As mentioned in connection with the intensity measurements, the heater on the mercury still was started at the same time as the lamp, so that the mercury was evaporating for some time before readings were taken. A set of intensity readings were taken first, followed by a set of photocurrent readings and the procedure repeated again during one setting. Care was taken to get a maximum for each reading and three or four readings were taken for each line. The photocurrent readings were made with a Cambridge and Paul Dolezalek quadrant electrometer. One pair of quadrants were grounded while the other pair were connected to the receiver. The sensitivity was 1250 mm. per volt with the scale at one and one half meters distance for a needle voltage of 92 volts. The photosurface was kept three volts negative to ground by dry cells. Taking electrometer readings with overflowing mercury has been tried before by McGougan[25] at Yale in connection with delta rays produced by alpha rays. Others have tried it also without success. They encountered the same difficulty which I did at first, namely, an erratic behavior of the electrometer as soon as the overflow commenced. I succeeded, however, in overcoming this completely and it should be worth while to describe that here. At first, when a glass cup and vertical outlet tube was used, it was thought, since the photochamber was shielded by a fine grounded wire screen completely surrounding it, that the trouble was caused by friction on the glass and by separation of the mercury into drops. Therefore, a change was made to the iron cup and the outlet tube of iron at 45 degress. The inlet tube of iron was fitted into a ground joint in the chamber, and cemented with a special high temperature cement furnished by the Mantle Lamp Company of America. The iron cup and tubes were carefully cleaned and oxidized before inserting. This cement was also used to attach

the quartz window. While the trouble was not eliminated, it was cut down considerably. A further search was made and at last it was found that the main source of trouble was in the mercury condensation tube and that the wire screen was not sufficient to cut down the induction effects and leakage. A large static charge is produced in the condensation tube when the mercury strikes the walls of the tube. Next the whole condensation tube and photochamber were closely wrapped by tin foil which was then grounded. The erratic behavior of the electrometer ceased entirely and the results followed quickly.

The electrometer readings were taken for periods of forty seconds for small currents and eight seconds for large currents, but were all reduced to an eight second basis. The mechanism for regulating the readings was a camera shutter fitted to the outlet hole in the box containing the mercury lamp, between it and the illuminator. The timing was done by means of a metronome which was frequently checked against a step watch. After the light was shut off at the end of each exposure, it always took about a minute for the reading to settle to a steady value. However, the electrometer leak which was always very small and taken with each reading, was always applied to the reading. The minimum readings between lines were taken again as in the intensity measurements and the same procedure was followed as mentioned there, namely, that of designating the stray light reading for each line as being that of the nearest minimum reading between the lines which could be definitely attributed to stray light. This is very important here for the stray light is composed of wave-lengths above and below that of the line itself.

Results

In every case, a deflection was obtained for 2700Å but none whatever for 2804Å, even when exposed for several minutes. In the case of 2754 Å, a very small deflection was obtained over a period of forty seconds of the order of 10 mm. but this was the deflection given by the stray light for that line so its net reading was zero. The rate of overflow could be slowed down a little bit and this condition still held so that for a maximum rate of intermittent overflow we were on the safe side. It is certain that the surface could not be contaminated in any way by this extremely short contact with the vacuum chamber. This is further proven by later attempts to give the surface

a chance to become contaminated without result for rapid intermittent flow. These results could be reproduced at will.

Table III gives a representative set of detailed photocurrent readings in mm.

Table III

Wavelengths in A		Time	Readings in mm.			Av.	Max. Dev. fr.Av.	Stray t = 8	Net Ave.t=8
Lines	Between Lines	Sec.	1	2	3				
2894		240	0	0	0				
2852		240	0	0	0				
2804		80	0	0	0				
2754		40	15	15	15	15.0			
	2725	40	17	17	16	16.7			
2700		8	12	12	12	12.0	0	3.6	8.4
2653		8	129	125	128	127.0	1.6	28.0	99.0
	2620	8	28	28	28	28.0			
2537		8	444	465	461	456.7	2.8	32.3	424.4
	2505	8	32	33	32	32.3			
2483		8	166	167	164	165.7	2.2	30.7	135.0
	2435	8	31	30	31	30.7			
2412		8	54	53	53	53.3	1.3	30.0	23.3
2400		8	101	103	102	102.0	1.0	30.0	72.0
2345		8	70	68	68	68.7	1.9		
2302		8	85	84	84	84.3	0.8		

The maximum deviation from average in the above table is less than 3 %. Thus the accuracy of measurement of the photocurrent is about the same as that of the intensity.

Following the method given by Millikan [19], the long wave length limit or threshold is obtained by plotting the photocurrent per unit intensity against the wave-length. The intersection of this curve with the wave-length axis gives the threshold value.

It must be born in mind that this intersection is governed by the points near the axis and not at all by those farther away and therefore, it is useless to make measurements far from the axis. In drawing the curves, use was made of regulation draftsman's long flexible guides and weights and the natural position of the guides in every case governed the direction. The curves were drawn on a large sheet of cross section paper 20 inches wide by 40 inches long, so as to be able to locate the intersection more carefully. In this way, a uniform method of drawing the curves was certain because the guides were in contact with the paper at only a few points and the friction of the guides with the paper was thereby reduced.

No mention is made by most investigators regarding stray light corrections to their readings and for that reason I have given all of the data and drawn the curves both ways, namely, for corrected and uncorrected values.

Figure 3 is for uncorrected values. While over thirty determinations were made, only four curves, taken at widely separate times during the investigation, are given here. Curve 1 was taken on August 22nd, 1923; curve 2 on August 27, 1923; curve 3 on September 3, 1923; curve 4 on September 12, 1923. All of the other curves, however, fall within the limits of these curves. The threshold from these curves is given as 2735A.

Figure 4 is for corrected values of the curves in figure 3. The threshold from these curves is given as 2745A.

Thus it can be seen that by this method of determination the stray light is practically without effect on the ultimate intersection excepting to serve as a criterion near the limit as to what readings to ignore.

The only other data that could be found for mercury was given by Derieux[26] and is merely qualitative. He writes on page 278 that the drops of mercury were sensitive to 2536A and not to 3126A, and that the lines between were too weak to give any readings. Klages[27] made an attempt to work on mercury in 1909 under poor experimental conditions, and the conclusions he drew are entirely discredited by later work.

C. - Study of the Effects of Dry Air, Oxygen and Hydrogen, upon the Current and Long Wave-Length Limit.

It had been noticed during the previous work that, when the surface was allowed to slow up and remain in the chamber a longer time, the line 2804A produced an effect. In order to see if the gases in the chamber had anything to do with it, the chamber was washed many times by different gases and the effect upon the current and long wave-length limit observed. No attempt was made to purify the gases by any extended process. There is no doubt that impurities may have been present but the behavior checks previous work and is therefore, presented here. Of course, with air, the experiments are accurate. These experiments are to be repeated with pure gases very soon.

Long Wave-length Limit

The threshold value was determined in the usual way at very low pressures. The tests were made in the order, air, oxygen, hydrogen.

Air

The air was slowly passed through three long drying tubes of calcium chloride and one of phosphorous pentoxide. The surface was stationary while this was being done. The pumps were then started and kept running continuously. The surface was started going rapidly and a test with line 2804A gave no photocurrent. The threshold determination is shown by curve I-A, figure 5. The surface was then stopped and as soon as this stage was reached determinations of the threshold were again made. The results are shown by curve II -A, figure 5. After the surface was again renewed and stopped and had been stationary for 15 minutes another determination, shown by curve III -A, figure 5, was made. The surface was again renewed, stopped, and left standing for 10 hours and curve IV -A, figure 5, was the result. The significance of these curves will be discussed later.

Oxygen

The oxygen was taken from a drum and passed very slowly through a long liquid air trap. That some hydrogen may have been present, there is no doubt,

but the action of the hydrogen as revealed by the next part, is very quick and the oxygen in time overcomes this. The surface was started going very rapidly after the pressure had been reduced and a determination of the threshold made as shown in curve I-O, figure 5. It will be seen that the presence of oxygen does not affect the limit for this rate of flow. The surface was stopped and another determination made which is not shown but was similar to II-A, figure 5. The surface was renewed and allowed to stand until by frequent trials it was found that the limit had gone down. This took about eight hours and curve II-O, figure 5 is the result. No further curves are given for oxygen since it behaved like air from that time on at these low pressures.

Hydrogen

The hydrogen was passed through drying tubes of calcium chloride and phosphorous pentoxide very slowly and then through a long liquid air trap. There could not have been very much impurity present in it finally. The pressure was reduced and the surface started going rapidly. A determination of the threshold made as shown in curve I-H, figure 5, shows that for this rate of flow, the presence of hydrogen has no effect upon the limit. The surface was then slowed down and readings taken until a change was noticed. This happened while the surface was still changing at a slower rate. It will be well at this time to introduce a notation to designate the rate of change of the surface. The rheostat governing the resistance of the heater for the still was marked 6,5,4,3,2,1,0. At position 6, the resistance was least and the distillation most rapid and at 0, the heater was off and the surface became stationary. It must be remembered that it always took a while before constant conditions for each setting were reached. The intermediate numbers represent proportionate rates of change of the surface. For position 6, the hydrogen shows no effect. The surface was then slowed down until for position 4, the next change was noticed as given by curve II-H, figure 5. After again running the surface rapidly and slowing down to position 2, curve III-H, figure 5, was the result. After remaining stationary for one half hour, curve IV-H, figure 5, was the result. This new limit held for several hours.

After ten hours the limit had gone back to nearly 2750A.

Significance of Curves

The new threshold value approximately 2910A could be reproduced again and again for air and hydrogen. This behavior of mercury and these gases is interpreted as follows: hydrogen is photoelectrically very active and raises the threshold value very quickly while air does so more slowly, but to the same value which would indicate that the hydrogen or some hydrogen like gas, (possibly nitrogen which was not tested), in the air was responsible for the initial behavior of air; oxygen is photoelectrically a retarding influence and takes a long time to show its effect. It is the oxygen of the air which is responsible for its later retarding influence. In all cases, it is important to notice that when the surface is changing rapidly, namely at position 6, no effect upon the threshold value is produced by the gases in the chamber and therefore, 2735A represents the true threshold value for mercury and is an intrinsic constant of the metal.

Photocurrents

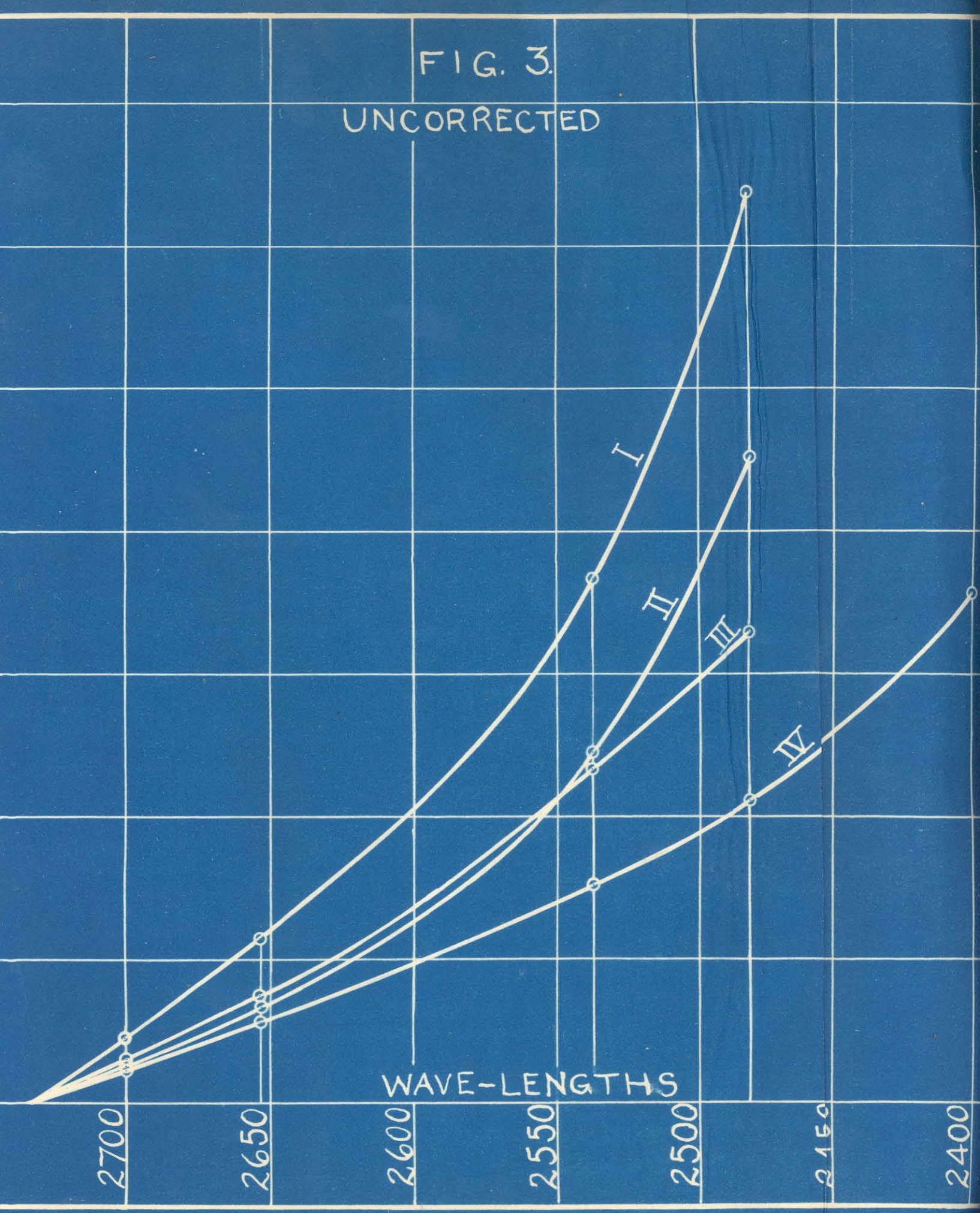
To study the effect of gases upon the photocurrents the same procedure regarding the preparation and introduction of the gases to the chamber were followed as before excepting that the pressure and rate of change of the surface were both varied. Higher pressures were used in order to get quicker effects in the latter part of this investigation for air and oxygen. All of the photocurrent readings were taken for forty seconds.

Hydrogen

Since it was found previously that hydrogen acted very quickly it was decided to work at low pressures and follow the variation of the photocurrents for the line 2804A because for a rate of change corresponding to position six this line was beyond the limit and it would be possible to watch the effect of the surface impurities more closely. In figure 6, the photocurrents are plotted against the time in minutes. In curve X-H, figure 6 the surface was started going very rapidly at

FIG. 3.

UNCORRECTED



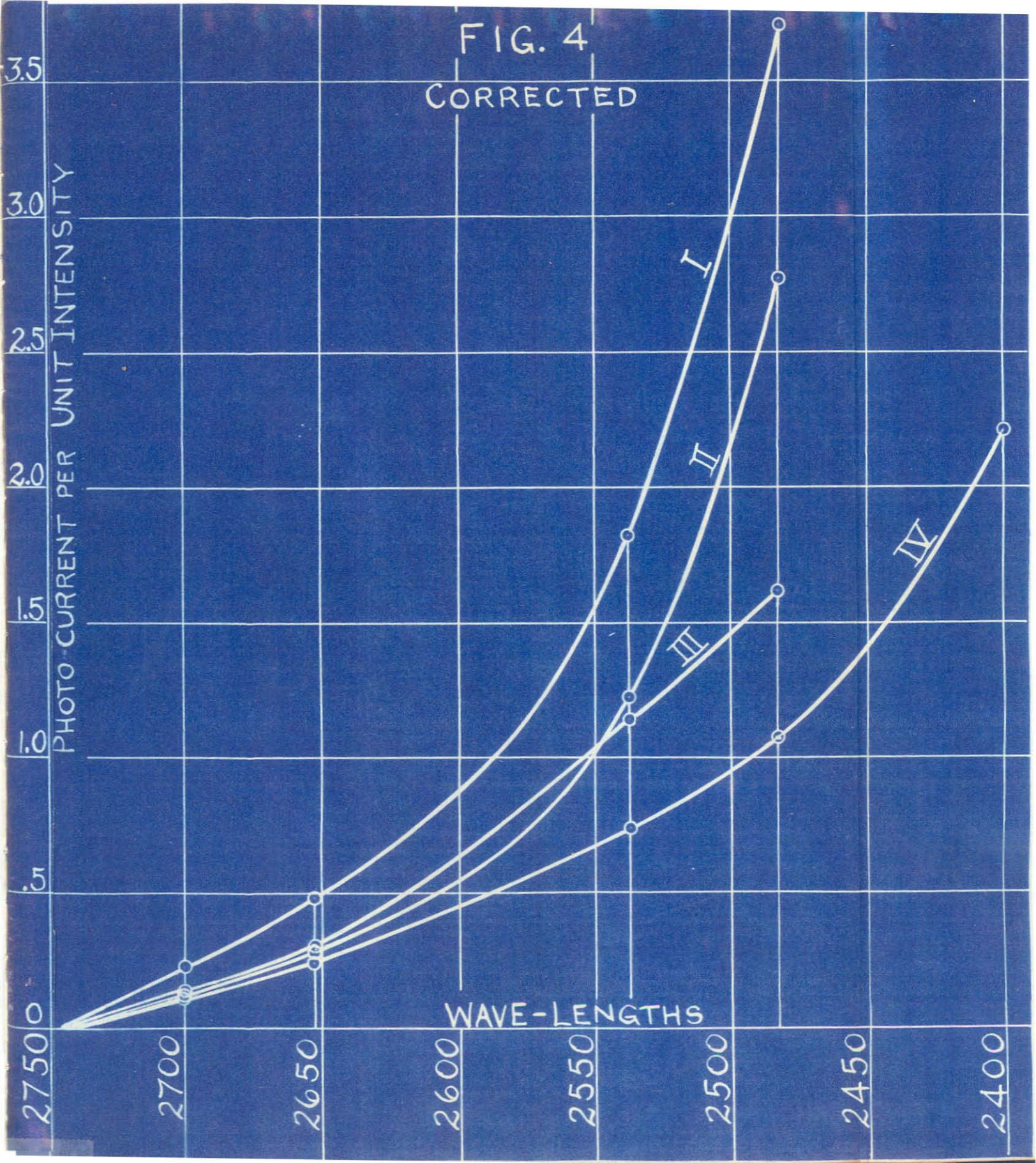


FIG. 4
CORRECTED
PHOTO-CURRENT PER UNIT INTENSITY
3.5
3.0
2.5
2.0
1.5
1.0
.5
0
I
II
III
IV
WAVE-LENGTHS
2750
2700
2650
2600
2550
2500
2450
2400

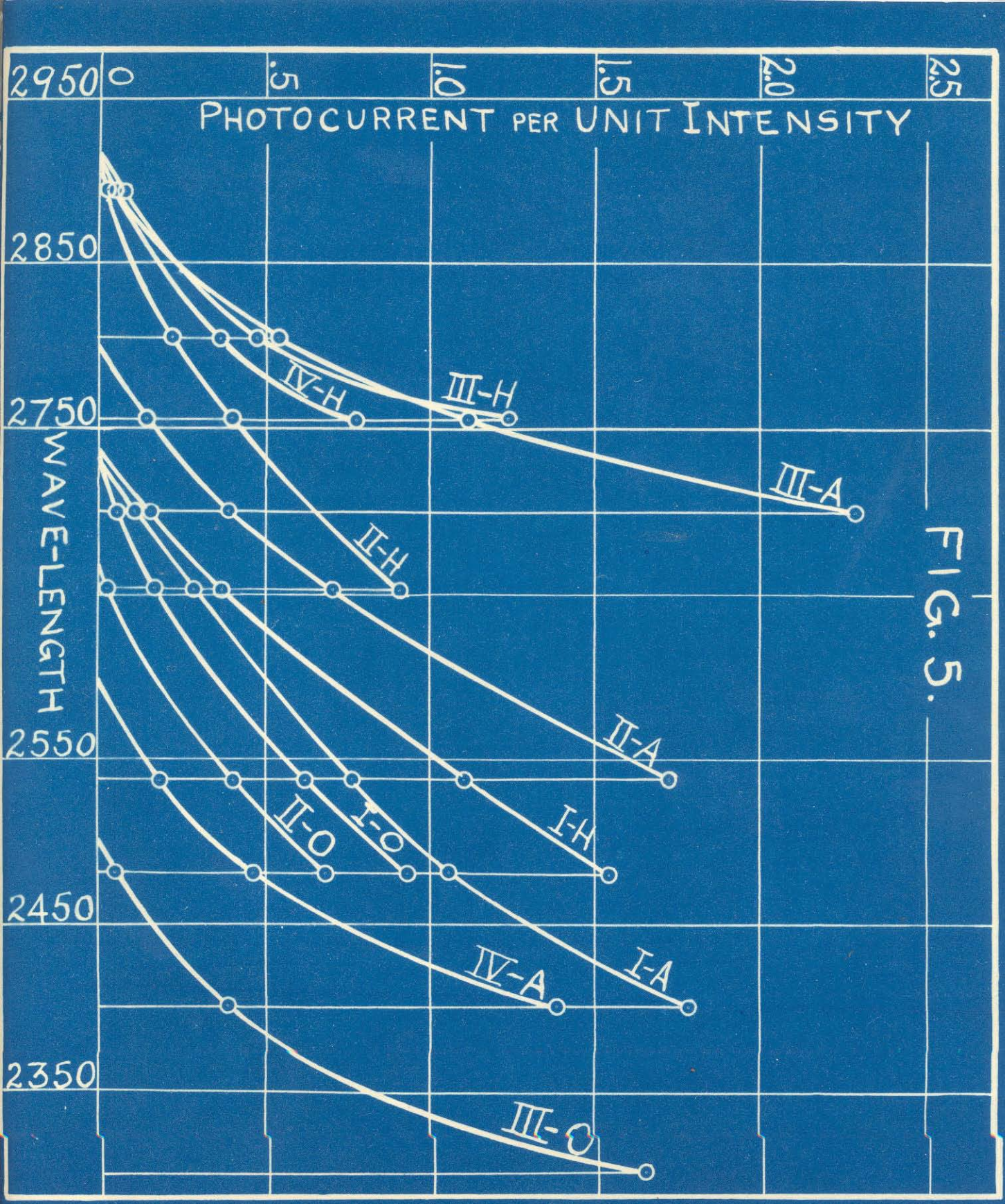

2950
0
.5
1.0
1.5
2.0
2.5
PHOTOCURRENT PER UNIT INTENSITY
2850
2750
2550
2450
2350
WAVE-LENGTH
IV-H
III-H
III-A
II-H
II-A
I-H
II-O
I-O
IV-A
I-A
III-O

FIG. 5.

position 6 and then the heating current set at position 2 and readings taken continuously. After the initial rise the photocurrents settled to a steady value. Then the surface was again speeded up to position 6 and the curve quickly shoots downward toward zero. Before it reached zero, the surface was slowed up again to position 2 and during this slowing up the curve again repeats its former behavior. Only two such repetitions on curve X-H, figure 6, are shown but this was carried on for four repetitions. In order to ascertain the cause of the sudden rise initially, since I suspected it had something to do with the rate at which the surface slowed up, curve XI -H, Figure 6, was taken. Starting at position 6, the current is zero. Then position 4 is set and the rate of slowing up is thus much less and the intial rise above a steady value is smaller. The steady value is again close to that in curve XH, figure 6. Then position 3 was tried and no change of steady value noted. Then by speeding up to position 6, the curve shoots down to zero quickly. The next trial was to do the opposite. This is shown in curve XII -H, figure 6. After position 6 with zero i_{photo} current the heater was set at position 1 and the initial rise of the curve was again large and then settled to a steady value a little lower than before. Then for position 6 the curve shoots to zero again. Many trials of this type were taken but only three extremes are shown. The others fall between these limits.

Air

The pressure for the work with air was of the order of 10^{-2} mm.Hg. Curve XIII -A, figure 6, is a typical curve. After a constant value for the line 2804A had been reached with the surface changing at the rate for position 1, the surface was allowed to slow down to zero and after a slight increase gradually the effect of the oxygen set in until after six hours the current fell to zero. This shows that an imperceptible film of oxygen gradually sets in and decreases the emission. For higher pressures the decrease was more rapid.

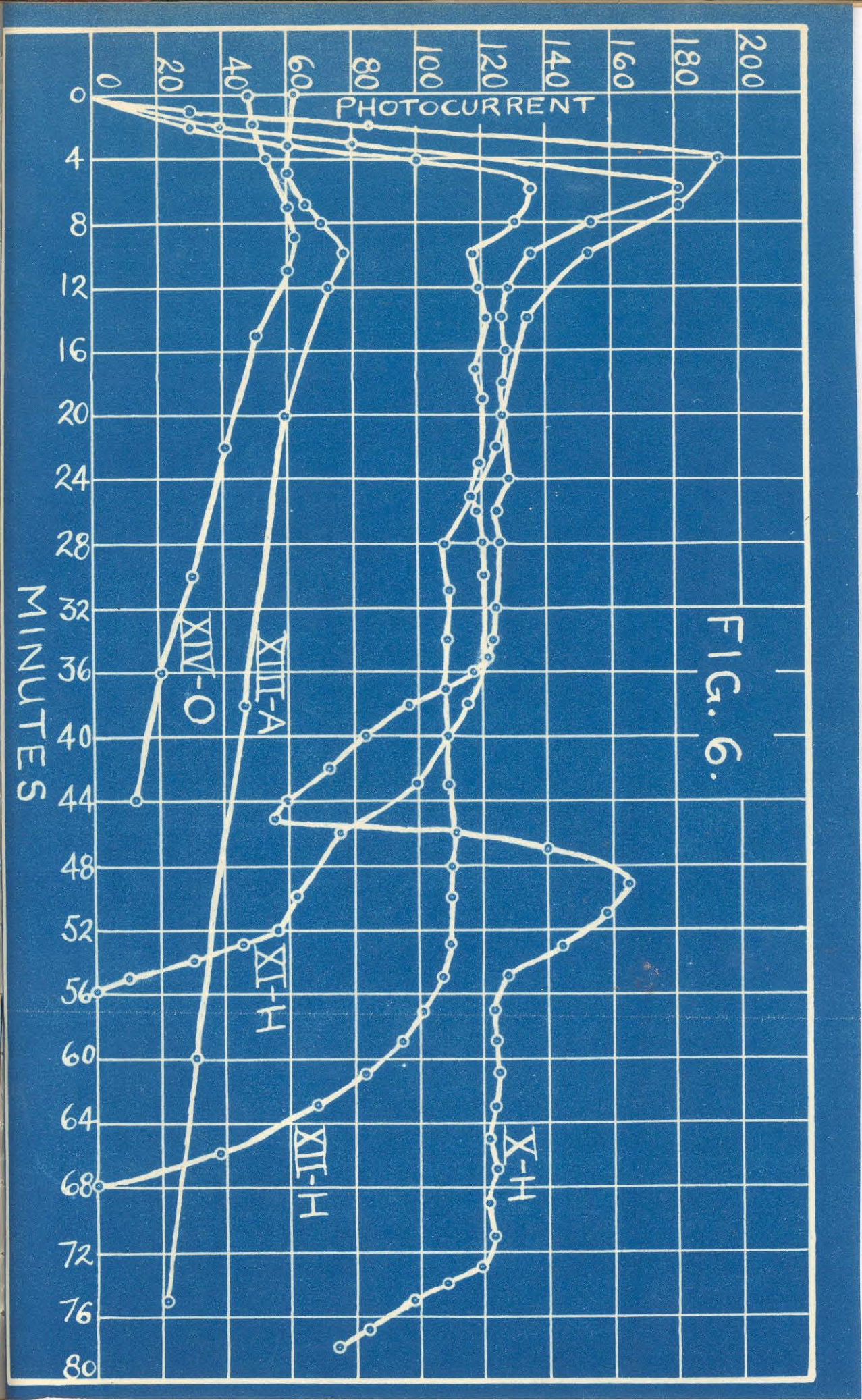

PHOTOCURRENT
0
20
40
60
80
100
120
140
160
180
200
MINUTES
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
80
XIV-O
XIII-A
XI-H
XII-H
X-H

FIG. 6.

Oxygen

The pressure for the work with oxygen was of the order of 1cm.Hg. Curve XIV-O, figure 6, is a typical curve. After a constant value for the line 2700 A had been reached when the surface was changing at the rate for position 2 the surface was stopped and readings taken at various intervals. When a zero value for the deflection was reached the next shorter wave-length always showed some deflection and it was followed up and this was carried on until no deflection could be obtained for the line 2303A.

It was always found that after the surface had been in contact with air overnight that no photocurrent readings could be obtained with line 2303A when the air was pumped out. This is no doubt due to an oxide film on the mercury. The full light of the lamp however, did give a deflection under these conditions.

Significance of curves

The curves clearly show that the formation of a gas layer and its variation do have a pronounced effect upon the photocurrent. They also show that it takes time for the gas layer to reach an equilibrium value as evidenced by the initial rise and a settling to a definite value. If a surface is not clean hydrogen raises the photocurrent considerably while oxygen lowers it.

Resume

The outstanding facts from the work with gases are:-

a. - The long wave-length limit for a rapidly changing surface is independent of the presence of gases in the photochamber over a considerable range of variation of intermittent flow.

b. - The long wave-length limit is shifted to new values, which can be consistently repeated, by the presence of gases if allowed sufficient time to reach an equilibrium state.

c. - The photocurrents are considerably affected by the presence of gases.

D. Discussion

A brief resume of the methods used by previous investigators will serve to point out the particular advantages gained by the present method of investigation.

A consideration of the reports of previous investigators reveals three methods used for removing impurities just before photoelectric determinations are made. They are as follows:-

1. - Mechanical removal of old surface.

2. - Heat treatment.

   (a) By heating entire chamber.

   (b) By local heating of specimen, in some cases up to the fusion point.

3. - Distillation.

The removal of gases and impurities at the surface of the material tested is not so easily accomplished by any of the above methods in the manner described in those reports. In the mechanical method, the previous history of the specimen used is important especially with active materials like the alkali metals. There is a serious doubt as to the condition of the surface at the time of measurement of photocurrent. The variation of the results for the threshold value by this method shows the lack of consistency of such determinations which is mainly caused by a certain time lag between the preparation of the surface and measurement of photocurrent. In the case of active materials, this would be a serious objection.

In the heat treatment method, part (a), the removal of gases is accomplished to some extent depending upon the temperature range used. This is limited, however, and other difficulties come in as pointed out by Tucker[17]. But again, the question of timelag between treatment and measurement of photocurrent comes in. The upper limit of temperature in this method has been around 200 degrees centigrade. In part (b) there are several things to be considered. The experiments of Hallwachs and his students and others in group 1 and especially referring to the recent experiments of Sende and Simon[9] and those of Suhrmann[10], the resultant

small photocurrent values for platinum have been explained by Welo[14]. Time of heating is the all important factor and Welo has shown that it requires long periods of continuous heating to completely remove the gases. Welo suggests that the policy of predicting an ultimate effect from past experience in these types of experiments should be done cautiously for if sufficient data is not obtained incorrect predictions may easily result. Another factor has been brought out by the work of Shenstone[28]. The usual rise in photocurrent for a particular wave length followed by a decrease as observed by many investigators including Hallwachs, Welo and others, is explained from the method used in degassing. Shenstone maintains that his experiments show that for experiments employing direct heating by an electric current, the rise is due to an electric current independent of its heating effect. It is entirely possible that the rate of removal of the emitted gases is not sufficient to prevent a pressure gradient between the surface of the metal and the chamber. It is then easily seen that during the interval between heating and measurement of photocurrent, the formation of a gas layer is entirely probable. Now the effect of this layer would depend upon the gases as well as the material composing the surface. No theory of metallic conduction has yet been proposed which would account for the effect Shenstone suggests. He could also say that the current had some effect on the gases in the metal which would account for the results. It is interesting also to point out that Borelius and Gunneson[29] have noted a periodicity in the gas emission from iron which has hydrogen and nitrogen occluded in it. The chemical change of the surface as understood in the ordinary sense is ruled out by recuperation curves obtained by all investigators.

The method of distillation accomplished the complete removal of occluded gases from the metal without doubt. However, it is important to safeguard the condensed metal from again absorbing gases and the formation of imperceptible fixed surface films which act like a new substance and effect the emission. There is undoubtedly a large pressure gradient next to the heated surface and only repeated distillation completely insures the purity of the metal. Some metals like aluminum form an imperceptible oxide which becomes fixed and is not easily broken up. The present method of

distillation provides for continual redistillation of the metal to be tested in the same apparatus and the distillation always takes place in the presence of an excess of the vapor of the metal.

Thus it is contended that the present method for determining the threshold value for mercury is free from the possible chances for contamination in previous experiments. The contimual distillation and the simultaneous measurement and presentation of surface has not been done before!

Theoretical Considerations

Millikan[30] has pointed out that the necessary conclusion from the constancy of stopping potentials is that each metal has a definite long wave-length limit and that furthermore, an agreement of photoelectric and thermonic work required to remove an electron from the surface by photoelectric means is given by the equation, expressed in volts and computed from the measured long wave-length limit as follows:-

$$h\nu_0 = \frac{300\ hc}{e\ \lambda_0 x10^{-8}} = \frac{1\ 23\ 4\ 5}{\lambda_0} = 4.52 \text{ volts}$$

where $e = 4.774x10^{-10}$; $h = 6.55 \times 10^{-27}$; $c = 3x10^{10}$; $\lambda_0 = 2735A.$

Millikan[30] has further pointed out that theoretically a consequence of the experiments on stopping potentials requires that the photoelectron must either be a free electron which receives a quantum of energy from the incident light, or be a bound electron which gets its energy from the atom, absorption by the atom of the incident radiation taking place. Barkla[31] from his work on X-rays has concluded that the latter view is the correct one. Millikan[30] presents the obstacles in the way of both of these theories.

Recently Whitaker[32] has proposed an atomic magnetic wheel model which accounts for energy exchanges between atom and electron. The angular oscillations (which really means radiations) are associated with the emission of an electron. W. Bothe[34] has also recently published a quantum theory of normal photoeffect. On the basis of conservation of energy and momentum he concludes that, in the interchange of a quantum of energy with the electron, it is essential that the electron be initially bound.

Very recently Jauncey [33] points out, on theoretical grounds, that the corpuscular theory of scattering has been worked out only for the case of a free electron, which results in no photoelectric effect. He points out that the electron must be initially bound for a photoeffect to take place. If the photoelectron is originally bound we would expect that the work required to remove an electron would increase with the energy of binding of the external loosely bound electrons although by so called collisions of the second kind an excited atom may also transfer its energy to the loosely bound electrons.

If the photoelectron is initially free we would expect the variation of photocurrent with temperature. This has not been tested over a wide range of temperature as yet and it may well be that the temperature effect when found will be a small one. In all probability the loosely bound external electrons are the ones which come into play and that the process is a twofold one, viz:- a sufficient absorption by the atom to free an electron and then an additional absorption of energy by the freed electron.

In conclusion I wish to thank Professor Millikan for suggesting that I work on mercury and for putting the facilities of the laboratory at my disposal. In particular, I am indebted to Mr. Ira Bowen for his kindly interest, to Dr. Edison Pettit for making the thermopiles, to Mr. Julius Pearson for helpful suggestions on the mechanical features of the apparatus, and to Mr. H. K. Dunn who helped me take many of the later readings.

Norman Bridge Laboratory of Physics,
Pasadena, California,
November 20, 1923.

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