PHOTO-ELECTRIC PROPERTIES OF SOLID AND LIQUID MERCURY: THE EFFECT OF TOLUENE ON LIQUID MERCURY; THE EFFECT OF TEMPERATURE ON SOLID AND LIQUID MERCURY

PHOTO-ELECTRIC PROPERTIES OF SOLID AND LIQUID MERCURY: THE EFFECT OF TOLUENE ON LIQUID MERCURY: THE EFFECT OF TEMPERATURE ON SOLID AND LIQUID MERCURY

A THESIS

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CONTENTS

ABSTRACT

Effect of Toluene on liquid Mercury: An apparatus is described which permits the measurement of the photo-electric emission and threshold for pure mercury contaminated with pure toluene vapor. It was found that the vapor from small amounts of toluene held at the temperature of liquid air produces no appreciable effect on the photo-electric behavior of pure liquid mercury. When, however, toluene vapor of considerably higher pressures (6mm and 30 mm) is introduced into the photo-cell, the sensitivity immediately increases and the threshold immediately shifts 100A toward the red. This shift in threshold is the same for both of the higher pressures and is independant of the time that the vapor is retained in the photo-cell.

A mercury surface which has been contaminated with toluene can be brought back to its normal behavior for pure mercury simply by connecting the photo-cell with the liquid air trap and pumps, and without the necessity of redistilling the mercury. The time of return to normal behavior varies between a few min-

utes and several days; the time increases both with the pressure of the introduced vapor and with the time that the vapor is held in the cell before pumping is begun.

The minimum cell voltage required for a saturated photo-current is increased by the introduction of vapor into the cell or by the formation of an adsorbed layer of vapor on the mercury.

<u>Effect of Temperature on Solid and Liquid Mercury:</u> Apparatus for measuring the photo-electric sensitivity at different temperatures is described. The range of temperatures was -190° to 25°. Monochromatic light was used and both the sensitivity and threshold were determined for various temperatures in this range. The threshold is independant of temperature. At room temperature it is 2735 10A, which is an independant confirmation of the value established earlier by Kazda and by Hales. At temperatures between -190° and -39°, where the mercury is in the solid phase, the threshold is at 2750 25A.

The photo-sensitivity of solid mercury is higher than that of liquid mercury, but it does not vary with temperature in the region below -39°. The increased sensitivity, without an accompanying shift of threshold toward the red, is attributed to an increase in the optical absorptivity, occuring when the mercury changes from the liquid to the solid phase. No evidence was obtained of a change in the crystal structure of solid mercury in the region of temperatures investigated.

I.

EFFECT OF TOLUENE ON THE PHOTO-ELECTRIC BEHAVIOR OF MERCURY

INTRODUCTION

The object of this investigation was to establish the effect on the photo-electric electron emission of mercury when the surface of mercury is contaminated with toluene vapor. Dunn (1) and Hales (2) found that mercury contaminated with stopcock grease had a much higher photo-sensitivity and a lower work function than had pure mercury. Poole (3) observed a similar result when mercury was contaminated with benzene. These results and those of other observers working with various metals indicate that certain organic substances tend to increase the photo-sensitivity of metals and to shift their photo-electric threshold toward the red end of the spectrum. This led to the present study with toluene, $C_6H_5CH_3$, which is the second memberof the benzene series, benzene itself, being the first.

It is now generally conceded that the photo-electric activity of a pure metal is an intrinsic property of the metal itself and that the confusing and contradictory results which are so often met with by workers in this field are due largely to the fact that metals have been used in the experiments which were not entirely free from contaminating gases and vapors. The most important experimental problem in photo-electricity then becomes that of finding means for obtaining very clean specimens of metal. Consequently, studies like the present one, where the contamination of a metal is deliberately brought about under controlled conditions, are concerned ultimately with the finding of experimental methods for eliminating contaminations. There is, however, a large possibility that such studies will also have the more direct end of furnishing evidence regarding the mechanism of photo-electricity itself and regarding the nature of adsorbed gaseous layers.

It is impossible to enter here into a lengthy discussion of the many experiments in which contamination effects (the so-called positive and negative fatigue effects) have been observed, for there exists an abundant literature regarding such phenomena. Many of the older experiments are described in the general treatises on photo-electricity, (4), (5), (11), and hence brief reference will be made here only to some of the most recent work.

It should be said here that the use of the term "fatigue" as equivalent in meaning to the expression "contamination effect" is confusing and inexact. Historically the expression "photo-electric fatigue" was invented to describe the phenomenon of a supposed fatiguing or loss of potency of a pure metal under the action of light. It is now regarded as certain that this phenomenon does not exist and that this so-called fatigue of a metal is a spurious effect due actually to the presence of impurities on and in the metal. It is well to keep in mind however, that the terms "fatigue" and "contamination effects" are used interchangeably even in the most recent literature.

BRIEF SUMMARY OF EXPERIMENTAL RESULTS ON THE EFFECTS OF CONTAMINATIONS ON THE PHOTO-ELECTRIC PROPERTIES OF METALS

A study of literature yields the following general facts regarding the so-called fatigue effects:

(a) Many substances do not alter the photoelectric properties of a metal. Helium, argon (2) and manthane (3), for example, apparently produce no effect on mercury.

(b) The action of a given kind of contamination on a given metal varies with the temperature, state of aggregation, time, thickness of the adsorbed film, etc. Welo (14) found that the effect of adding gases after outgassing platinum by heating is dependent on the particular sample of platinum in use. The writer has found that contamination effects in mercury depend upon the state of aggregation of the mercury.

(c) A single contaminating substance may afford more than one mechanism for changing the photoelectric properties of a metal. Thus Leupold (8) found that the presence of ammonia considerably increases the photo-sensitivity of platinum as compared with the presence of air; but in the region of an absorption band the ammonia produces a marked decrease in the number of photo-electric electrons emitted. From this one can see that at least two mechanisms are operative here and that it is possible for the work function of a metal to be lowered by the presence of a contaminating substance, while at the same time the photo-sensitivity of the metal to certain wave-lengths may be diminished. Ordinarily, the sensitivity rises when the work function is lowered.

(d) A given contaminating substance does not affect the photo-electric properties of all metals in the same way. For example, DuBridge (6) and others conclude that hydrogen strongly increases the photo-current from platinum, while Hales (2) found that hydrogen has no effect whatever on the photo-electric properties of liquid mercury.

CURRENT THEORIES OF THE CAUSES OF CHANGES IN THE PHOTO-ELECTRIC PROPERTIES OF METALS

According to Hallwachs, the possible causes for fatigue, are: (a) direct action of the light; (b) oxidation of the surface or chemical action of the surrounding gas on the photo-active metal; (c) forming of electrical double sheets; (d) physical changes in the metal itself, such as a roughening of the surface occurring with time; (e) adsorption and absorption of gas molecules and gaseous ions. The first four causes given here unquestionably influence the photo-electric phenomena in many cases, but, as pointed out by Predwoditelow and Witt (9), Allen (3) and others, they cannot be accepted as a complete explanation. The fifth cause, the effect of gases, seems to be the one which usually explains the whole variety of so-called fatigue phenomena.

It should be pointed out that in experiments involving the introduction of a contaminating gas into a photo-electric cell, there also arises the possibility of a spurious decrease in sensitivity due to a lack of saturation of the photo-current. Ives, Olpin and Johnsrud (15) show that the accelerating potential required for saturation depends on the pressure of the residual gas in the photo-electric cell.

Many attempts have been made to formulate explanations of the effects of gases on the photo-electric properties of a metal. Predwoditelew and Witt (9) have proposed a theory of fatigue which is in good agreement with their experiments and which establishes a connection expressed in the form of an equation, between the decay in the photo-current from a metal and the quantity of gas adsorbed. The theory is based on these assumptions: (a) the greater part of the light energy absorbed by a metal is consumed in increasing the average energy of resonators and not in the loosening of electrons; (b) only the outer-most layer of metal is photo-active; (c) as a consequence of adsorption of gas there is produced a situation which is analagous to that of the formation of a new substance on the surface, this substance having a new mean prototype of resonators and different photo-electric properties.

Wiedmann and Hallwachs (7) attribute the initial low sensitivity observed for fresh platinum to the presence of an adsorbed layer of electro-negative gases which hinders the escape of electrons; the rapid rise in sensitivity which is observed when the platinum is heated is due then to the removal of this layer. They conclude further that gases which are absorbed in the body of the platinum in some way aid in the ejection of electrons and that the removal of such gases by heating produces the observed gradual lowering of the photo-current. DuBridge (6) has found evidence of an increase in sensitivity due to the formation of a surface layer of gas on a cool platinum surface which previously had been outgassed.

Mendenhall (16), using evidence furnished by the phenomena of electronic bombardment, concludes that two changes take place during the heat treatment of a metal being prepared for photo-electric purposes; one is the outgassing, which is complicated but which in general reduces the number of electrons; the other is the devolpment of a surface structure, a crystallisation, which tends to increase the number of electrons. He believes that it is the undetermined combination of these two effects which is responsible for the difficulty of securing reproducible and stable limiting surface conditions.

THE WORK OF KAZDA, DUNN, HALES AND POOLE ON LIQUID MERCURY

Kazda (10) working in this laboratory, made the first successful measurements of the the photoelectric behavior of mercury. He made use of a flowing surface of mercury which had just been condensed form the vapor state. A given particle of mercury was in contact with the residual gases present in the highly evacuated photoelectric cell for less than a second, a time too short for the surface to become contaminated to an appreciable extent. Kazda in this way found the threshold value for liquid mercury at room temperature to be 2735±10A., which corresponds to a value of 4.52 volts for the work function.

It was found by Kazda (10) that as soon as the mercury surface was allowed to slow down and become stationary, the threshold value immediately changed. This effect he attributed either to contamination or to some kind of change in molecular arrangement occurring when the surface came to rest. With the apparatus as he had designed it, Kazda was unable to show definitely that the threshold value of 2735A was characteristic of stationary as well as of flowing mercury.

The photo-electric cell designed and used by Kazda, and later also used by Dunn, was much like the one shown in Fig. 1. The photo-electric cell is near the center of the figure and on the right of it is the mercury still. The mercury evaporated at a rate which depended upon the current applied to the heater. It condensed inside the water jacket and fell into the tube below, the fall being broken by a perforated glass plate. It then flowed through a small tube and up into a small iron cup, where it presented a surface. It then overflowed down an inclined iron tube and returned to the boiler of the still. Above and around the iron cup was a copper oxide receiver, closed above except for a slit to admit radiation. The receiver caught the electrons ejected from the mercury, the latter being maintained at a constant potential of about 3 volts negative to ground. The receiver was connected by means of a shielded wire to a Dolezalek quadrant electrometer, which was operated at a sensitivity of about 1100 mm per volt for a scale distance of 1.5 meters. Except where otherwise mentioned the apparatus was constructed of Pyrex glass. The photo-electric cell and still were connected through a liquid air trap to two stages of condensation pumps.

It is of importance to note that in this original apparatus a stopcock, lubricated with stopcock grease, was situated between the liquid air trap and the pumps, and that the iron cup and quartz window in the photo-electric cell were held in place by a high temperature cement.

The source of light was a quartz mercury arc, which was operated at constant voltage, current and temperature. The light passed through a camera shutter into the collimator of a Hilger monochromator. From the monochromator the light passed through an adjustable quartz lens, by which it was focussed on the slit of the receiver in the photo-electric cell. The relative intensities of the lines emitted by the arc were measured by means of a vacuum thermocouple and a D'Arsonval galvonometer of sensitivity of the order of 10^{-9} amperes.

The long wave limit or threshold was found by plotting the photo-current per unit intensity against the wave length. The intersection of this curve with the wave length axis gives the threshold value. Kazda took into account corrections for stray light and for the details of this procedure his paper should be consulted.

Dunn,(1) working with the same apparatus, found that if the mercury surface was brought to a standstill, the threshold changed in 8 minutes from the value of 2735A for flowing mercury to one of 2850A. Eighteen hours later, the surface in the meantime having been left undisturbed, the threshold had moved in the direction of shorter wave length to a value of 2770A, which is still above the value for the flowing surface. After standing in the high vacuum for both 66 hours and 114 hours, however, the threshold had receded to 2680A, a value considerably below that for flowing mercury.

Using a radioactive leak in conjunction with the electrometer, Dunn also studied the variations with time of the photo-sensitivity to the mercury arc line 2653A. Eight minutes after the mercury surface in the photo-cell had become stationary, the sensitivity rose to a maximum of nearly five times that for the flowing surface. It then began to decrease, rather rapidly for about fifty minutes, and then more slowly. At the end of 66 hours it was about one-third the value for flowing mercury. When the surface was again brought into motion by starting the still, the sensitivity quickly rose to a value considerably above the normal value for the flowing surface, then began to decrease, and finally reached the normal value in several hours after the surface had been set into motion. When this normal value was obtained, it was found to be independent of the rate of flow.

Dunn concluded from these results that there were at least two stages to the process of contamination of the mercury surface. He suggested that two different impurities could be responsible for the phenomena observed, the one acting very quickly and raising the threshold, the other acting more slowly and lowering it. He also suggested that the phenomena could be attributed to a single impurity on the mercury surface, a single layer of molecules of this impurity facilitating the release of electrons from the mercury and a number of layers of the impurity hindering their release. Whichever of these two explanations was the correct one, it was certain at least that the second stage of the contamination was quickly removed when the surface was set into motion, while the first stage, which resulted in an increase in sensitivity, held more tenaciously.

Dunn next tried the effect on both flowing and stationary mercury of removing the liquid air from the liquid air trap. The results he obtained were rather complicated but interesting. From them he was able to conclude that the fivefold increase in sensitivity which always occurred when the mercury was first brought to rest was due to a substance condensed in the liquid air trap and having a melting point near $0^{o}C$. It also seemed probable that the substance responsible for the subsequent slow fall in sensitivity was not a substance condensed in the liquid air trap.

Since stopcocks were a part of the apparatus as designed by Kazda, Dunn next tried the effect of introducing the vapor of stopcock grease at room temperature into the photo-electric cell. Stopcock grease is composed of vaseline and rubber. He found that the introduction of the stopcock grease produces a very large increase in the sensitivity.

Hales (2) completely rebuilt the apparatus with new materials. In doing so he introduced two important modifications:(a) the stopcocks on the low-pressure side of the diffusion pumps were replaced by mercury cut-offs and (b) the high temperature cement used in the old apparatus was entirely eliminated from the new one. Whenever, for one reason or another, air was admitted to the apparatus, it had to come through the stopcocks which were still retained on the high pressure side of the diffusion pumps.

After two months of pumping, this new apparatus was found to be so free from contaminations that the photocurrent from the stationary mercury remained constant for a day. It was also found that contamination of the mercury resulting when the mercury was allowed to remain stationary for several days could be removed in an hour, where-as in the old apparatus it took three or more hours for the flowing mercury to rid itself of the contamination.

From these results Hales concluded that two impurities had been responsible for the effects obtained with stationary mercury in the old apparatus. He believed that the stopcock grease had produced the rise in sensitivity, for by eliminating the stopcocks on the low pressure side of the apparatus, the rate of rise of sensitivity was reduced to an almost negligible amount. As for the subsequent decrease in sensitivity which always occurred in the old apparatus, and which did not occur at all in the new one, this he attributed to the high temperature cement. With the apparatus as he had designed it, Hales was able to obtain Kazda's value of 2735±10A for a stationary surface of mercury as well as for a flowing surface. The apparatus as Hales had designed it provided an excellent means for the study of the effects of contaminating substances on the photo-electric behavior of mercury. In investigations of the so-called fatigue effects it is desirable to work with a stationary surface and it is essential that the standing surface be free from impurities other than those deliberately put into the photo-electric cell for purposes of study.

The apparatus as designed by Kazda had been used by Kazda for the study of the effects of air, oxygen and hydrogen upon the mercury and by Dunn for the study of the effects of stopcock grease and of hydrogen. The results which they obtained can be learned from their published papers (1D,1). Investigations of the effects of contaminating substances were made with Hales' apparatus by Hales himself and, later, by Poole and then the writer. Hales (2) studied the effects of hydrogen, helium, argon, water vapor, nitrogen and oxygen. Poole investigated the effects of methane, oxygen, oxygen illuminated by ultraviolet light, oxygen combined with water vapor, carbon dioxide, carbon monoxide, air, benzene and alcohol. The results obtained by Hales and Poole are summarized in Table I.

EFFECT OF TOLUENE ON MERCURY: PLAN OF WORK AND GENERAL PROCEDURE

The plan of study of the effects of toluene on the photo-electric behavior of mercury divides itself into three parts:

(a) A study of the relation between the density of the toluene vapor admitted to the cell and the photo-electric current from the mercury. Changes in the density were accomplished by changing the temperature of the tube containing the supply of toluene. The three temperatures used were that of liquid air,

TABLE I

Substance	Observer	Pressure During Exposure	Length of Exposure in Hours	Threshold Shift
Hydrogen	Hales	30 mm	48	None
Helium	Hales	.005 mm		None
		10 mm		None
Argon	Hales			None
Water	Hales	.001 mm		None
		.05 mm	20	To 2800A
Nitrogen	Hales	100 mm	24	None
Oxygen	Hales	50 mm	18	To 2555A
		50 mm	72	To 2560A
	Poole	20 mm	20	None
Oxygen & Ultraviolet Light	Poole			To 2660A
Oxygen & Water	Poole	20 mm	17	To 2565A
Methane	Poole	4 mm	17	None
Carbon Dioxide	Poole		2	None
Carbon Monoxide	Poole	18 mm	16	None
Air	Poole	15 mm	14	None
Benzene	Poole	Room temp.	4	To 2830A
Alcohol	Poole	Room temp.	3	To 2550A

The threshold for clean mercury is 2537 10.

that of melting ice and room temperature. The mercury in the photo-electric cell was in every case held at room temperature.

(b) A study of the relation between the photo-electric current and the time that vapor of a given density was permitted to remain in contact with the mercury surface. An attempt was also made to determine the least time that the toluene vapor must be in contact with the mercury in order to produce an appreciable effect on the photo-current.

(c) A study of the changes taking place in the photo-current as time progressed after toluene vapor of a given density had been in contact with the mercury for a given time, the mercury in the meantime not being disturbed.

The general procedure was to pump out the photo-electric cell while the mercury in the cell was being distilled and then, without introducing any contaminating vapor, to bring the mercury surface to a standstill and make a control run over the same period of time as would later be consumed in making a series of observations with toluene in the cell. During the period of the control run the toluene was in an auxiliary apparatus, separated from the main apparatus by a mercury valve or cut-off, and this auxiliary apparatus was being evacuated and thoroughly flushed with toluene by means a separate set of vacuum pumps. After the control run the mercury was again distilled. The mercury surface was then brought to rest and, with the tube of toluene at a given temperature, the mercury valve between the supply of toluene and the photo-electric cell was opened. In the meantime the tube connecting the photo-cell with the main pumps and liquid air trap was closed by another cut-off, this to prevent the condensation of toluene vapor in the main liquid air trap. After a predetermined interval of time the source of supply of toluene was disconnected from the cell and the toluene was removed by connecting the cell with the main pumps and liquid air trap.

EFFECT OF TOLUENE ON MERCURY: APPARATUS AND EXPERIMENTAL METHOD

The apparatus, Fig.1, was essentially the same as that used by Hales (2) and by Poole (3). It differed in design from the apparatus devised by Kazda (10) in that all the stopcocks on the low pressure side of the pumps had been replaced by mercury valves or cut-offs and in that the high temperature cement in the photo-electric cell had been eliminated. The apparatus and technique used for introducing the contaminating substances differed in minor details from that employed by any of these workers. A general view of the apparatus is shown in Fig. 2.

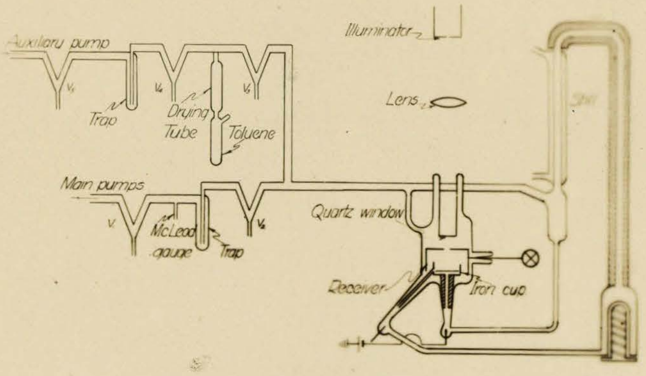
Auxiliary pump
V_1
Trap
V_4
Drying Tube
V_3
Toluene
Illuminator
Lens
Main pumps
V
McLeod gauge
Trap
V_2
Quartz window
Receiver
Iron cup

Fig. 1.

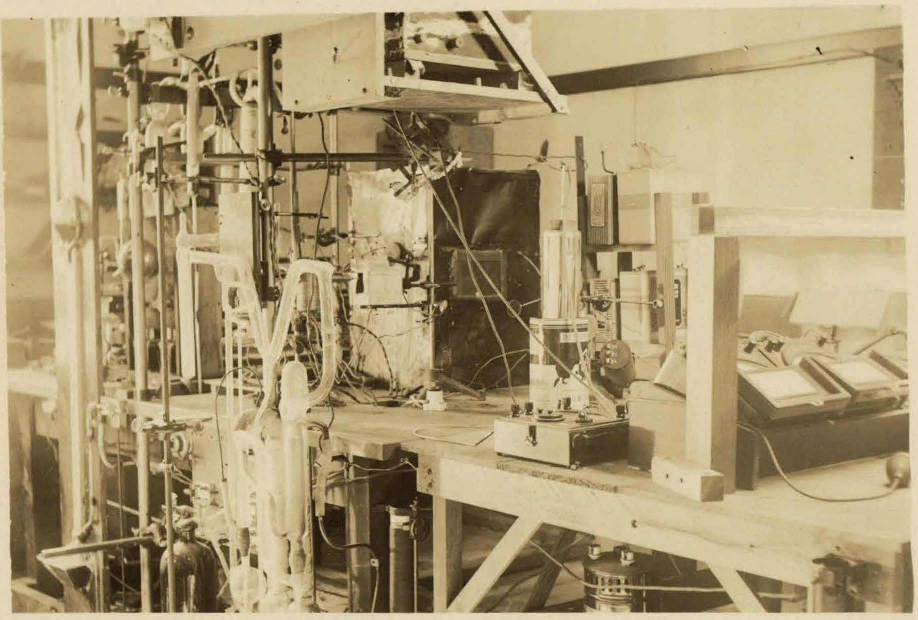

Fig. 2.

The photo-electric cell consisted of a Pyrex vessel in which a shallow iron cup, 2 cm in diameter, was mounted on a cone of invar so shaped as to fit in a ground glass joint in the vessel. Through the bottom of this cup there passed a small bore Pyrex tube connected to the condenser of a mercury still. When the still was operated, which was not the case during the time when the readings were being made, freshly condensed mercury overflowed from the iron cup into an inclined iron tube connected to the boiler of the still. The mercury was kept at a negative potential of magnitude sufficient to produce a saturated photo-current. The receiver of the photo-electric cell consisted of an insulated oxidised copper Faraday cage with a slit in the top to admit the light; the receiver was located just above the iron cup and was connected with one pair of quadrants of a Dolazalek-electrometer. The other pair of quadrants of the electrometer was grounded. A quartz window was located just above the slit in the receiver, it being sealed directly onto a graded quartz to Pyrex seal. Both the photo-electric cell and the mercury still were connected through two mercury valves V1 and V2, Fig. 1, and a liquid air trap to two single stage diffusion pumps and an oil pump.

The source of illumination was a quartz mercury arc lamp enclosed in an asbestos-lined box. The light from the lamp passed in turn through a camera shutter, a Hilger monochromator, an adjustable quartz lens, and then through the quartz window and receiver onto the mercury in the photo-electric cell. The lamp always was allowed to run for a period of one and one-half hours before observations were begun, it then being operated at 91-93 volts, with a current of 2.4 amperes and an ambient temperature of 202-204°C.

The apparatus used in introducing the toluene vapor into the cell is also shown in Fig. 1. A mercury valve V3 and a drying tube containing phosphorus pentoxide were situated between the photo-electric cell and the vertical tube containing the toluene. The toluene tube also was connected through two mercury valves V4 and V5 and a liquid air trap to an auxiliary set of pumps and an oil pump. Thus the apparatus containing the toluene could be evacuated independently of the apparatus containing the photo-electric cell. The two valves V1 and V5 were kept closed during such times as the pumps were not being operated, this being done to keep the vapor of stopcock grease out of the main parts of the apparatus.

The toluene, $C_6H_5CH_3$, used in these experiments was obtained from a very pure source furnished by

Dr. A. K. Brewer, of this laboratory. It was also distilled twice by the writer.

Measurements of the photo-electric current were made by the ballistic method (13). The needle of the electrometer was kept at a constant potential of 90 volts, the sensitivity for a scale distance of 150 cm being about 1100 mm per volt. In making the calculations of the specific photo-electric currents, that is, the current per unit intensity of the light, use was made of the calibrations of the relative intensities of the various lines of this lamp made by Hales (1). Threshold values were determined in the usual manner.

In every case data first were obtained for the uncontaminated mercury, this being done just before the toluene was admitted to the photo-electric cell and under the same working conditions as were to be used in studying the effect of admitting the contamination. After completing this control run the mercury was again distilled so that a fresh surface of mercury would be present in the cell. The valve V2 was then closed and then the valve V3 opened, thus admitting the toluene vapor to the cell; the pressure of this vapor was determined by the temperature of the tube containing the toluene. After a measured length of time valve V3 was closed and Valve V2 opened, thus connecting the cell with the liquid air trap and main pumps and separating it from the source of supply of the vapor. In the intervals between and after these operations, the photo-electric currents were measured; in cases where the sensitivities were changing slowly, these measurements were made for several wave-lengths, so that a threshold curve could be plotted, while in other cases, where rapid changes of sensitivity were taking place, the behavior of the sensitivity for a given wave-length was all that could be observed.

EFFECT OF TOLUENE ON MERCURY: EXPERIMENTAL RESULTS

Toluene at temperature of liquid air: the introduction into the photo-electric cell of the extremely small amount of vapor given off from solid toluene kept at the temperature of liquid air resulted in an apparent lowering of the photo-sensitivity of the mercury to the lines 2537A and 2653A. The vapor pressure of the toluene at this temperature is about 0.005 mm. Some typical results are contained in Table II, where the ratios of the photo-currents from contaminated and from pure mercury are given. The two values forming a ratio were observed at corresponding times.

The first two sets of readings in Table II were made during the same run and without disturbing the

TABLE II

Time of Observation	Ratio of Currents	
	2537A	2653A
Just after the mercury had been exposed ½ h. to toluene vapor.	0.96	0.94
After 75 minutes of pumping.	0.90	0.87
Just after the mercury had been exposed for 2 hours to toluene vapor.	0.92	0.93
After 30 minutes of pumping.	0.92	0.90
After 8½ more of pumping.	0.96	0.97

mercury surface by causing it to flow. The last three sets of readings were obtained during another run, but under similar conditions. It is to be noted that shutting off the supply of toluene and connecting the photoelectric cell with the pumps and liquid air trap produced no consistent changes in the ratios of the photo-currents, even after 8.5 hours of pumping. This means that it was impossible to eliminate the cause of the decrease of the photo-current simply by connecting the cell with the liquid air trap and pump.

All of Table II was obtained with the mercury in the photo-cell held at a negative potential of 8 volts. In order to find if the apparent decrease in sensitivity was due to a lack of a saturated photo-current, the negative potential of the mercury in the photo-cell was increased. It was found that the photo-current increased slightly with an increase in the cathode potential. This showed conclusively that the most, if not all, of the apparent decrease in sensitivity was a spurious effect, due to the fact of the photo-current being rendered unsaturated when the pressure in the photo-cell was increased by admitting toluene vapor. This explanation is not incompatible with the observation that it was impossible to bring the mercury back to normal behavior by connecting it with the pumps and liquid air trap. Such connection served chiefly to cause the toluene to condense in the liquid air trap, without reducing the pressure of the vapor appreciably.

Thus it is seen that extreme care must be taken to have a saturation photo-current in experiments which involve an increased pressure in the photo-cell. This is a precaution which has not always been observed in fatigue experiments and such negligence possibly is responsible for many spurious results.

In addition to the data of Table II, observations were made of the effect of the toluene on the photo-sensitivity to the mercury arc lines 2700A, 2754A, and 2803A. The last two lines are <u>beyond</u> the threshold for clean mercury, while the first is quite close to the threshold; moreover, these lines, especially the first two, have relatively low intensities. Because of these facts and because of the smallness of the effect of such minute quantities of toluene, the observed changes were found to be within the experimental error. There was some evidence, however, that the toluene produced a slight shift of the threshold, and that this shift was toward the red.

One may then conclude that the vapor from toluene held at the temperature of liquid air produces no appreciable effect either on the photo-sensitivity or on the

the work function of mercury. Thus a liquid air trap affords adequate protection against the presence of small amounts of toluene in a mercury photo-electric cell.

Toluene at $0^{o}C.$: The pressure of the vapor introduced into the photo-cell was in this case about 6 mm. Fig. 3 shows the effect of introducing toluene of this pressure on the sensitivity of the mercury to line 2653A. This series of observations was made with the mercury at a constant potential of 3 volts negative to ground and after the mercury had been freed from occluded gases by repeated distillation in a high vacuum for several days. At the time zero the heater on the mercury still was disconnected and the surface of mercury in the photo-cell thus allowed to come to rest. Readings of the photo-sensitivity of the clean mercury to line 2653A were then made until the end of 66 minutes (first dotted ordinate), at which time the photo-cell was cut off from the main pumps and liquid air trap and was connected with the source of supply of toluene. The toluene was allowed to remain in contact with the mercury for 14 minutes (during the interval A, Fig. 3). During this time two readings were taken which were considerably lower

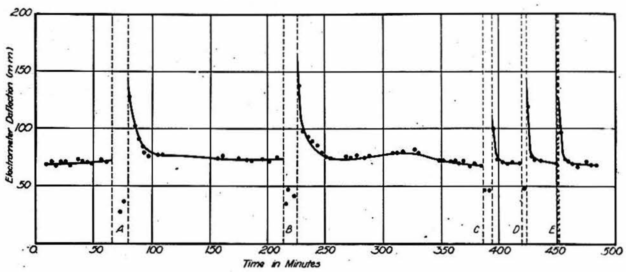

Fig. 3.

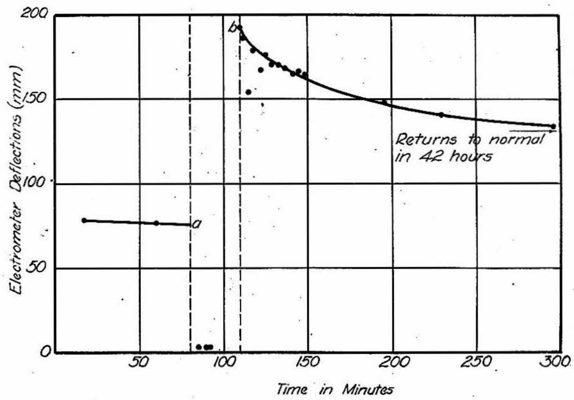

Fig. 4

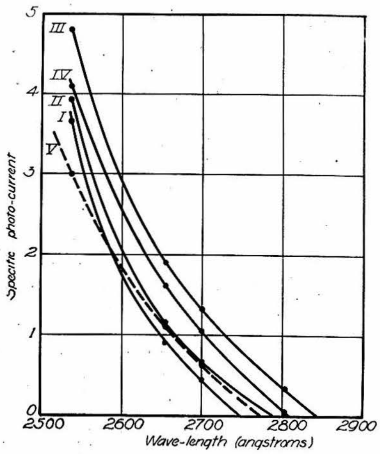

Fig. 5

in value than the readings made before the toluene was introduced. At the end of the 14 minutes of exposure to toluene (second dotted ordinate, Fig.3), the source of supply of toluene was cut off and the photo-cell was connected to the main pumps and liquid air trap. The photo-sensitivity was now found to be increased considerably above the value for clean mercury, the initial reading after connecting the pumps showing a 75% increase. Since there was necessarily some delay in taking this reading and since the approximate nature of the curve always obtained after withdrawing the supply of toluene has been well established by many series of observations similar to the one shown in Fig. 3, it would seem safe to extrapolate the curve backwards and to conclude that in the case under consideration the photo-current was at least doubled by the introduction of the toluene. A further examination of Fig. 3 shows that as time progressed after connecting the pumps the sensitivity rapidly returned to its characteristic value for clean mercury. It is important to note that this was accomplished simply by connecting the photo-cell with the pumps and liquid air trap, and without disturbing the mercury surface by causing it to flow or by heating it. This process of introducing toluene vapor and then withdrawing it was repeated a number of times (B,C,D,E, Fig.3) without in the meantime disturbing the mercury surface. In each case the behavior was the same; upon withdrawing the toluene the sensitivity was found to have increased and as time progressed it returned to its normal value. This occurred even when the vapor was allowed to remain in the photo-cell only 55 seconds, the sensitivity at the end of that time again being about double that for the uncontaminated mercury. At the end of about 325 minutes, Fig.3, a tendency toward an increase in sensitivity was noticed; an examination of the Dewar flask on the main liquid air trap showed that the supply of liquid air in it was low; when this was replenished the sensitivity soon began to come down.

Besides the series of observations described above, data were also obtained for cases where the toluene was allowed to remain in the photo-cell for periods of one-half hour and one hour. In these cases it was possible to make observations of the effects due to six different mercury arc lines and thus to determine the effect of the toluene on the long wave-length limit.

As soon as the toluene vapor was admitted to the cell, the sensitivity of the mercury to the lines 2537A and 2653A began to decrease markedly, thus exhibiting an effect similar to that shown in Fig.3. At the same time the sensitivity to 2803A changed from zero (this line being well beyond the threshold for clean mercury) to a value such as to give an electrometer reflection of 16 mm per minute for a one minute exposure to the light. The sensitivity to this line then began to decrease slowly.

Upon connecting the photo-cell with the pumps and liquid air traps, a procedure which almost immediately reduced the pressure of the toluene vapor in the cell from 6mm to 0.005 mm, the sensitivity to 2537A and 2653 A rose suddenly to a value considerably above that for clean mercury, while the electrometer deflection for 2803A dropped suddenly to 4 mm per minute.

In an attempt to find the cause of this reduction in sensitivity to certain lines and a simultaneous increase in sensitivity to another line during the time that the vapor was in the cell, the negative potential of the photo-electrically active mercury was increased. This was found to increase the photo-current and thus again the apparent drop in sensitivity appears in its true light as a spurious effect due actually to an unsaturated photo-current. The presence of the toluene had in fact increased the sensitivity of the mercury and had produced a decided shift of the threshold towards the red; that this shift is not due simply to the change in the applied field is clear from the fact that the sensitivity near the threshold increases with the admission of toluene, even when the applied field is held constant. Upon connecting the photo-cell with the pumps, the effect begins to disappear, the rate of disappearance being very rapid during the first few moments of pumping. This is particularly true of threshold values, for the sensitivities to lines very close to the threshold decrease most rapidly. Hence it appears that it is a very difficult matter to obtain a true index of the magnitude of a contamination effect by making measurements after pumping has begun.

Unfortunately, it is also difficult to obtain consistent electrometer readings while the vapor is in the cell. Attempts to obtain a saturated photo-current by increasing the cathode potential often resulted in leakage and an erratic electometer needle. However, by combining the data obtained under such unfavorable conditions with those obtained later, when the cell is connected with the pumps, it is possible to make fairly accurate threshold determinations.

The shift in threshold toward the red which existed while the toluene was in the photo-cell was of the order of 100A, for both the case where the vapor remained in the cell for 30 minutes and the case where it remained in the cell one hour. When the photo-cell was connected with the pumps and liquid air both the threshold and the sensitivities began to return to the value for clean mercury, but now the time of return was as much as 6 hours, as compared with the short times required in the cases represented by Fig. 3.

None of the series of observations made for toluene at this pressure reveal any dependence of the magnitude of the rise of sensitivity or of the shift in threshold upon the time of exposure of the mercury surface to the toluene. The magnitude of the increase was of the same order regardless of whether the toluene remained in the cell one minute or several hours.

On the other hand, the rate at which the effect disappeared with pumping did depend upon the time that the vapor was allowed to remain in the cell. The shorter the time of exposure of the mercury to the toluene, the more quickly did the mercury return to its normal behavior with pumping.

Toluene at room temperature: The pressure of the toluene vapor admitted to the photo-cell was in this case about 30 mm or five times greater than when the toluene was held at 0°C. Fig. 4 represents a typical result obtained when the vapor of this pressure was introduced into the cell for a period of 30 minutes. At the time zero the heat was turned off on the mercury still so that the mercury surface in the photo-cell was brought to rest. Two readings were taken for the clean mercury and then at the point a, Fig. 4, the photo-cell was cut off from the main pumps and liquid air trap and the toluene vapor was admitted.

At the point b, Fig. 4, 30 minutes after the toluene was first introduced, the source of supply of toluene was cut off from the cell and the latter was connected with the main pumps and liquid air trap. The sensitivity was now found to have been increased about two and one-half times the value for clean mercury. As time progressed the sensitivity decreased and gradually returned to the normal value, but the modified mercury surface produced by the contamination was now much more persistent than for vapor of lower pressures. In the case of Fig. 4, 42 hours were required for the photo-sensitivity to return to the value characteristic of clean mercury. It is significant, however, that finally it did return to this value, and that this return was brought about without the necessity of redistilling the mercury.

Because of the greater persistency of the effect for vapor of this pressure, the character of the sensitivity curve obtained just after connecting the pumps becomes more evident (b, Fig.4.). This initial erratic behavior of the sensitivity probably occurs also in the case of lower vapor pressures, but it happens too quickly for observation. This gives further weight to the contention that data obtained while the cell is connected with the pumps may lead to erroneous conclusions regarding the magnitude of the effect. Fig. 5 offers a further illustration of this point. Curve I is a threshold determination for clean mercury. Curves III, IV, and V, in the order named, represent threshold determination made as pumping progressed after a 30 minute exposure to toluene at room temperature; Curve III was obtained soon after the cell was connected with the pumps, and Curve V 18 hours later. Curve II, on the other hand, was obtained immediately after a 30 minute exposure to toluene at 0°C.

During the time that toluene of 30 mm pressure was in the photo-cell, the mercury showed a shift of threshold toward the red of the same order of magnitude as that produced by vapor of 6 mm pressure, namely, 100A. Changing the time that the vapor was allowed to remain in the cell apparently had no effect on the magnitude of this shift, but did change the rate at which the long wave-length limit returned to normal with pumping.

A comparison of the results obtained for different pressures shows that the rate at which the effect of the contamination disappears with pumping varies with the pressure of the vapor, as well as with the time of exposure. The greater the time of exposure and the greater the pressure of the vapor, the more persistent is its effect on the mercury.

CONCLUSIONS

(a) The presence of small amounts of toluene in a liquid air trap has no appreciable effect on the photo-electric behavior of mercury.

(b) The presence in the photo-cell of toluene vapor having a pressure between 6 mm and 30 mm causes the long wave-length limit of the mercury to shift 100A toward the red. This shift exists when the potential of the mercury is only 3 volts negative, although it is then difficult to measure because of the lack of saturated photo-currents.

(c) The shift in the threshold occurring while the vapor is in the photo-cell is independent of the pressure of the vapor, for the range of pressure 6 mm to 30 mm. In this connection it should be said that the work of Frazer, Patrick and Smith (19) shows that the thickness of the adsorbed film of toluene on a plane surface is never greater than unimolecular, even at saturation pressures.

(d) The shift in threshold is independent of the time that the vapor is held in the photo-cell, at least for times ranging between 55 seconds and several days. The effect seems to reach its maximum value almost immediately.

(e) A mercury surface which has been contaminated with toluene can be brought back to its normal behavior for clean mercury simply by connecting the photo-cell with the liquid air trap and pumps, and without the necessity of redistilling the mercury. Thus the effect apparently is due to an adsorbed layer of toluene, and not to an absorption of the toluene by the mercury.

(f) The rate ~~mt~~ which the effect disappears with pumping depends both on the pressure of the vapor and on the time that the vapor is retained in the cell before pumping is begun. The time required for the mercury to return to its characteristic behavior for clean metal varies between a few minutes and several days, the time increasing with increased exposure to the toluene and with greater vapor pressures.

(g) Poole (Table I) found that after a 4 hour exposure to benzene at room temperature, the long wave-length limit of mercury shifts 95A toward the red. Thus toluene and benzene produce effects of the same nature and order of magnitude.

(h) When vapor is introduced into the photo-cell and when adsorbed layers of gas are present on the metal, caution must be observed to see that the applied voltage is sufficient for a saturated photo-current; otherwise very misleading results may be obtained.

(i) Further experiments of this nature should be conducted with a photo-electric cell so designed that reliable measurements can be made during the time that the contaminating vapor is in contact with the metal. The design of the cell should be.such as to make possible the use of high applied voltages without resultant leakage. Means should also be provided for measuring the absorption, if any, which the ultra-violet light undergoes when it passes thru the volume of vapor and through the layers of vapor adsorbed on the window and metal of the photo-cell. In this connection, one should consult the work of Leupold on the effect of ammonia on platinum (8).

II

EFFECT OF TEMPERATURE ON THE PHOTO-ELECTRIC BEHAVIOR OF SOLID AND LIQUID MERCURY

INTRODUCTION

The photo-electric properties of mercury at room temperature have been studied extensively, but with the exception of some unpublished work by R. Pohl, there has been no attempt to study the photo-electric behavior of the metal at low temperatures.

In experimental work on the relation between the photo-electric effect and temperature, an attempt is made generally to gain information regarding one or both of the following points: (a) the question of the existence of a true temperature effect, that is, whether a clean metallic surface suffers changes of its photo-sensitivity and threshold with changes in temperature; (b) the behavior of the photo-electric properties ofa a metal as it passes through the melting point and through other transition points, such as a crystallographic changes.

The general consensus of opinion has been that there does not exist a true temperature effect of appreciable magnitude. This conclusion is based on the results of many experiments. Yet at the same time there is considerable evidence in the literature for the existence of the effect. It is impossible to give any adequate survey of the literature in this paper, but some mention will be made of the more recent work, with particular regard for results which are positive in character.

Ives (20) and Ives and Johnsrud (21) find that the variation of photo-current with temperature in sodium, potassium and rubidium is continuous and without abrupt changes. Smooth surfaces of potassium exhibit a much greater variation than rough surfaces. With a smooth surface the effect for yellow light amounts to a variation of ten to fifteen times between room temperature and the temperature of liquid air. Hornbeck (22) confirms the existence of a considerable temperature effect for potassium and, in addition, finds a sharp discontinuity in the photo-current at about -80°C. This he associates with a change in the crystal structure of potassium which is known to occur at this temperature. Ives and Johnsrud failed to find such a discontinuity, although they knew of Hornbeck's results and attempted to duplicate the experimental conditions under which he worked.

Nielsen (23) concludes that for aluminum the photo-current due to 2573A remains constant within ½% as the metal is cooled from 400°C. to 100°C. He has discussed the influence of a change of temperature upon the threshold frequency on the basis of Richardson's theory and arrives at the result that the temperature variation of the threshold is proportional to the Thompson coefficient. According to this, the threshold frequency should be practically independent of temperature, since the Thompson coefficient is always very small. Hall (24) has obtained an expression for the work done in removing an electron froma metal which indicates that the work should diminish with rise of temperature.

Wehnelt and Seiliger (25) have observed that the emission curves for copper and silver exhibit kinks at the melting point which indicates that the emission work of the liquid state is less than that of the solid. They conclude that the number of free electrons is reduced in passing from the solid to the liquid approximately in the same ratio as the resistances of the metals increase.

DuBridge (6) finds that for thoroughly outgassed platinum the photo-current is independent of the temperature up to 500°C. Beyond this temperature the photo-current rises, first slowly, then more rapidly, until at 1200°C it is about double the value at room temperature; at the same time, the threshold shifts slightly to the red. DuBridge concludes that this is a genuine temperature effect characteristic of the metal itself and due to the increase in the thermal energies of the "free"electrons which may become appreciable at high temperatures.

Thermal collisions also become an appreciable factor at temperatures between absolute zero and room temperature, according to Suhrmann (26).

Warner (27), working with tungsten, finds the photo-current and threshold frequency constant up to 1050K. At this temperature the thermionic emission becomes measurable and at the same time the photo-current begins to increase slightly, showing a 14% increase at 1160K.

Goetz (28) (29) has made an extensive study of the thermionic emission from iron, silver, gold and copper at transition and melting points. He discusses the known changes in the electrical properties of metals at these points with respect to conductivity and to thermal and photo-electric effects. Caldwell (30) finds that for iron the variation in the photo-current with temperature is complicated. In the region 475°-768°C there is a decrease in the photo-sensitivity with increase in temperature, and this Caldwell recognizes as a pure temperature effect; there are also variations in the sensitivity which can be associated with the transitions from alpha to beta and from beta to gamma iron.

Pohl, of Göttingen, found no change in the long wave-length limit of mercury as it passed from the liquid to the solid state, but because of the difficulties inherent in photo-electric experiments at low temperatures, he concluded that mercury was not a suitable metal for studying variations at transition and melting points. Consequently he soon terminated the work and did not publish any results (34).

The problem of mercury at low temperature has a particular point of interest due to the fact that there is evidence of a change in crystal structure somewhere in the region between -78°C and -115°C. Allen and Aminoff (31) find one structure at -78°C, while McKeehan and Cioffi (32) find a different one at -115°C; Ewald and Hermann (33) conclude from these results that the two very different determinations can be explained by an allotropic change in the region in question.

THE PHOTO-CELLS

Two different types of photo-cells were used during the course of the experiment.

Photo-Cell Number One: This cell was made of Pyrex and was of the design shown in Fig. 6. Mercury entered the cell through a side tube and formed a pool on the Pyrex bottom of the cell. A tungsten wire made contact with the mercury and served as a means of keeping it at a negative potential. The receiving electrode consisted of a flat circular disk of tungsten, 3 cm in diameter, which contained a narrow slit through which the light could pass. A tungsten rod, welded to the disk with nickel and passing out of the cell through a horizontal side tube 12 cm in length, served as a support for the disk and as a conductor to the electrometer. Just above

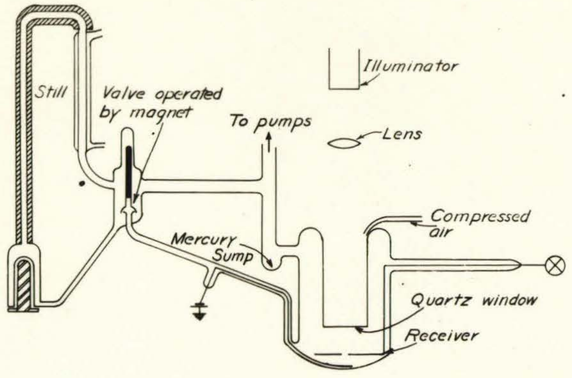
Still
Valve operated by magnet
To pumps
Illuminator
Lens
Compressed air
Mercury Sump
Quartz window
Receiver

Fig. 6

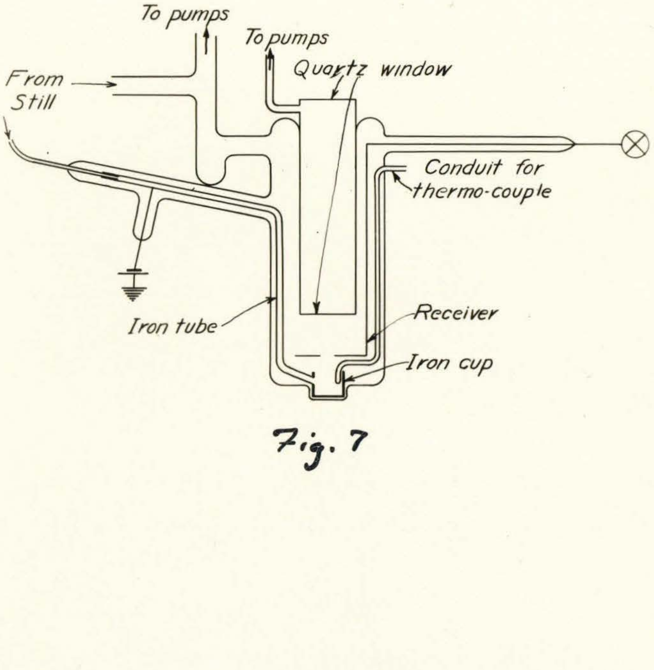
To pumps
To pumps
Quartz window
From Still
Conduit for thermo-couple
Iron tube
Receiver
Iron cup

Fig. 7

the receiver was a quartz window, which was sealed directly onto a graded quartz to Pyrex seal. The outside of the window was kept clear of moisture by blowing dry air upon it. The cell was shielded by covering its outside walls with a conducting layer of powdered graphite. The graphite first was moistened with a little water glass and water and was then applied to the Pyrex with a brush. When the cell was baked, the graphite formed a hard layer which did not scale or rub off appreciably. The water glass, which indeed was used very sparingly, apparently did not weaken the Pyrex, for no breaks occurred in it during two months of continuous evacuation.

Temperatures were measured by means of a spot welded constantan v. steel thermo-couple and a Model 3355 Rawson multimeter. The junction was enclosed in a glass tube placed close to the pool of mercury, but not touching it. It was not imbedded in the mercury because of the belief, based on the experiences of other experimenters, that a glass tube imbedded in a very clean liquid metal will be fractured when the metal solidifies . Later this was found not to be the case, at least for mercury. Before calibrating the thermo-couple, it was subjected repeatedly to the lowest and highest temperatures to which later it would be exposed.

Defects in Cell Number One: Experiments with the cell just described revealed the following defects and these were taken into account in designing an improved cell:

(a) Since the junction of the thermo-couple was not in contact with the mercury, a temperature difference of about 5° existed between the mercury and the junction. While it is possible to make an approximate correction for this difference, it is desirable to avoid the necessity of it by placing the junction in the mercury.

(b) The use of a current of compressed air as a means of keeping the cell window free from moisture is impracticable. Despite the fact that the air was washed successfully in potassium hydroxide and sulphuric acid, and then was passed through a long drying tube containing calcium chloride and glass wool, it still contained traces of oil and moisture. Consequently, continual care was required to keep the cold window of the cell clean.

(c) A strong drift of the electrometer needle occurred whenever the temperature of the cell was changing rapidly. This drift was not due to leakage but, as subsequent tests showed, at least partly to the presence of thermo-couples in the receiver circuit. The receiver had been built entirely of tungsten for the express purpose of avoiding thermo-electric effects, but account was not taken of the fact that tungsten sheet and tungsten rod contain different amounts of thorium. It is possible that the nickel used in welding the rod to the disk was a factor in producing the effect; also, there is some evidence that the sudden cooling or warming of the glass walls of the cell produce effects of an electrical nature.

(d) When the mercury was first admitted to the cell from the still, no electrometer deflection could be obtained upon exposure of the mercury to monochromatic light, even when the light was of as short a wave-length as 2400A, and the applied voltage was as high as 100 volts. During this time the electrometer would show a strong drift in the direction it would have if the anode were being charged positively. When the evidence of a photo-current did begin to appear, which occurred in a time varying between 15 minutes and several hours, this current was very weak and could not be rendered saturated by applying 100 volts to the cathode. The current then rapidly became stronger and finally could be made saturated by a potential of about 20 volts. Experiments showed that a saturated current could be obtained within a few minutes of the time of admission of the mercury, provided the mercury first was exposed to the intense polychromatic light of a naked mercury arc lamp. The apparent explanation of the effect is that the mercury produced a large positive charge on the glass walls of the cell when it flowed in through the Pyrex tube and that this charge caused the electron current to be deflected away from the receiver. By exposing the mercury to the intense "white" light of the mercury arc a large photocurrent was produced which soon dissipated the static charge on the glass. An alternative explanation would be that a pure metal has no photo-electric properties and that the photo-current appears after the surface either has become contaminated or has been modified in some way by exposure to the light. But such an explanation is untenable, as many conclusive experiments have shown; and besides, there remains the fact, observed both by Kazda and by the author, that a photocurrent is obtained <u>immediately</u> upon admitting mercury to the cell, providing the mercury is made to enter through a metallic conduit.

The few minutes delay incurred in exposing the mercury to the naked arc is probably of no moment, as experiments showed that the photo-current at room temperature was constant over a long period of time. However, it is desirable to be able to make measurements immediately after the metal has been condensed from the vapor state.

<u>Photo-Cell Number Two</u>: This cell, Fig. 7, was designed to eliminate the troublesome features of the first cell. It differed in the following important respects: (1) the junction of the thermo-couple used for measuring temperatures was imbedded in the surface of the pool of mercury; (2) compressed air was abandoned as a means of keeping the cell window clear of moisture. Instead, an additional quartz window was fastened to the upper end of the cell, and the space between the two windows was evacuated; this arrangement not only prevented moisture from forming on the windows, but improved the thermal insulation of the cathode of the cell; (3) the receiver, or anode, was made from a single sheet of tungsten, to reduce thermo-electric forces. The disk of the anode was larger than in the first cell, it being 4 cm in diameter, while the slit in this disk was made somewhat smaller; (4) the pool of mercury forming the cathode was contained in an iron cup 2.5 cm in diameter, the mercury being admitted to the cup through an iron tube which

passed out through an opening in the wall of the cell. The mercury was fed into this tube through a delivery tube from the still. Both the delivery tube and the iron tube were surrounded by a larger Pyrex tube which was sealed to the remainder of the apparatus; this arrangement made it possible to dispense with a graded seal from iron to Pyrex.

APPARATUS AND METHOD

Surrounding the photo-cell was a tightly built galvanized iron oven. This oven was used for baking the cell. It contained drying material and was grounded, so that it also served to retard the collection of moisture on the cell when the latter was cooled, and as an electrostatic shield. The point where the tungsten lead to the mercury cathode entered the cell was kept dry with a small heating coil. The tungsten lead from the anode to the electrometer emerged from the cell at a point outside the oven; this point was kept dry by calcium chlorid contained in the metal shield leading from the cell to the electrometer. Fig. 8 is a general view of the apparatus with the oven removed; Fig. 9 is the same view with the oven in place.

The mercury first was purified by the method of Appen- I and then was plased in the still, Fig. 6, which formed and integral part of the apparatus. It was distilled

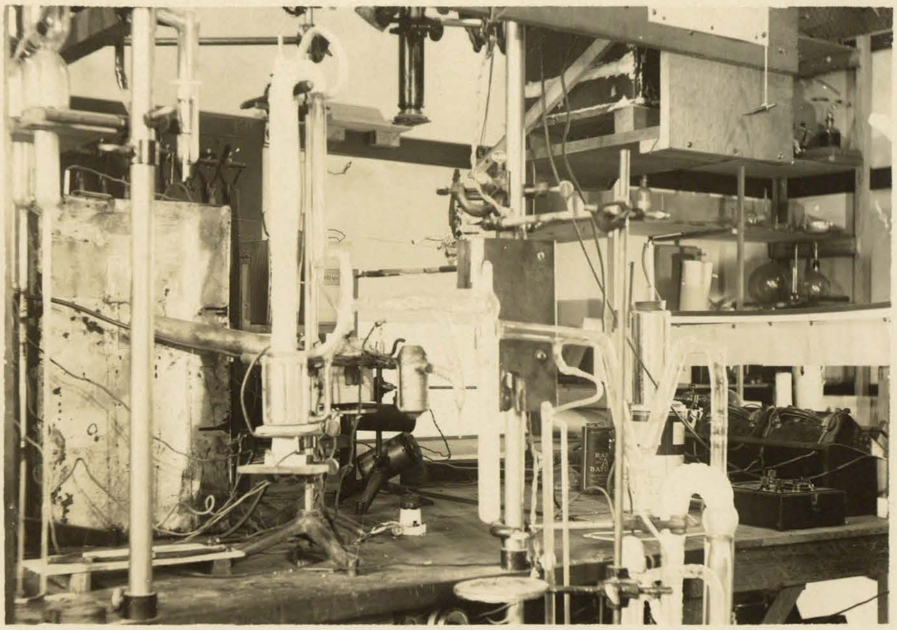

Fig. 8

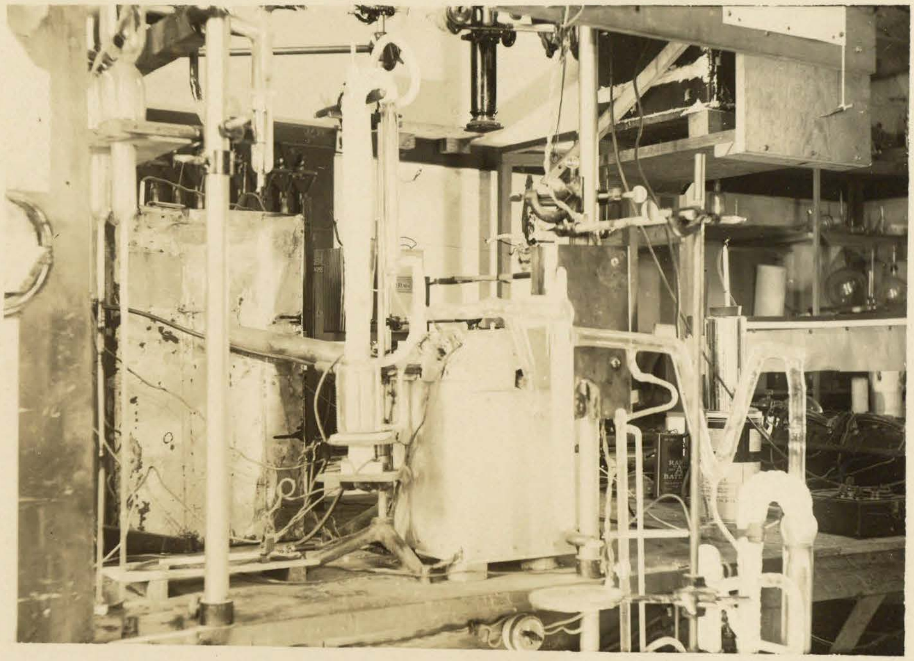

Fig. 9

repeatedly in high vacuum to remove occluded gases. The photo-cell was baked at 350°C, after which the mercury was admitted to it through the magnetically operated valve shown in Fig. 6. When it was desired to remove the mercury from the cell, the latter was baked until all of the mercury had distilled over into a sump provided for this purpose.

The photo-cell and still were connected through a large liquid air trap to two stages of condensation pumps and a Hyvac pump. Nothing but Pyrex was used in the glass system and there were no greased, waxed or cemented joints on the high vacuum side of the pumps. All measurements were made with a vacuum better than 10^{-6} mm, as indicated by a McLeod gauge.

The freezing of the mercury in the cell was accomplished with a cooling agent contained in a specially designed wide-mouthed Dewar flask which slipped over the bottom of the cell. When the flask was filled, the cooling agent covered the walls of the cell to a distance of 7 cm above the surface of the mercury. The various agents employed were liquid air, mixtures of liquid air and alcohol, and mixtures of carbon dioxide and ether, depending upon the temperature and rate of warming desired.

The source of illumination was a quartz mercury are lamp enclosed in an asbestos-lined box. The lamp was operated at 91-93 volts and 2.4 amps. Use was made of Hales' intensity calibrations for this lamp(2). The light from the shutter passed in turn through a camera shutter, a Hilger monochromator and an adjustable quartz lens; the lens focussed the light on the slit in the cell anode.

Photo-currents were measured in the manner described on page 20 of this report. All currents reported are saturation values. The mercury cathode in the photo-cell was maintained at various negative potentials, but for the most part at 20 volts negative to ground.

AN INDEPENDANT DETERMINATION OF THE THRESHOLD FOR MERCURY AT ROOM TEMPERATURE

Although Photo-Cell Number One proved to be unsuitable for work involving temperature variations, its unique design provided the means for making an independant determination of the threshold for mercury at room temperature. This cell differed in several important respects from the cells used by Kazda, Dunn and Hales. Each of these previous workers had used apparatus of essentially the same design, except that Hales' apparatus did not contain stopcocks or cemented joints. In each case the mercury forming the cathode of the cell was contained in an iron cup, and the anode of the cell was made of oxidized copper (Fog.1). In the present work, on the other hand, the mercury of the cathode was not in contact with iron, but with Pyrex glass and tungsten wire, and the anode of the cell was made of tungsten (Fig. 6).

Using Cell Number One (Fig. 6), the threshold for mercury at room temperature was found to be at 2735 10A, which is the value found by Kazda, Dunn and Hales. This constitutes the first independant check of the work of Hales with a stationary surface of mercury. Moreover, it independantly confirms Hales' conclusion that stationary and flowing mercury have the same threshold.

THE THRESHOLD FOR SOLID MERCURY

Determinations were made of the photo-electric threshold for solid mercury, for various temperatures between -190° and the melting point. For all temperatures in this range, the solid mercury exhibited a threshold of 2750 25A, as compared with the value 2735 10A at room temperature. No definite systematic shifts of the threshold were observed, except that mercury held at a low temperature for times exceeding about one hour showed a small shift toward the small wave-length region. The results given in the next section of this report show that such shifts are due to contamination.

THE PHOTO-ELECTRIC CURRENT AS A FUNCTION OF TEMPERATURE

Measurements were made of the photo-electric emission as a function of temperature, for each of the lines 2537A, 2653A and 2700A. Results typical of about ~~sisxty~~ sixty curves made for each of these lines are shown in Fig. 10. The arrows indicate the direction of temperature variation. The time required for the mercury cathode to warm up from the temperature of liquid air to room temperature, or for the cooling process over the same range of temperatures, was varied between one hour and twelve hours.

The results for increasing temperatures may be summarized as follows: (a) beginning with the temperature of liquid air, the sensitivity is practically constant until the region ca. -125° is reached, where a slight decrease begins to occur. This decrease is most pronounced near the melting point. Between

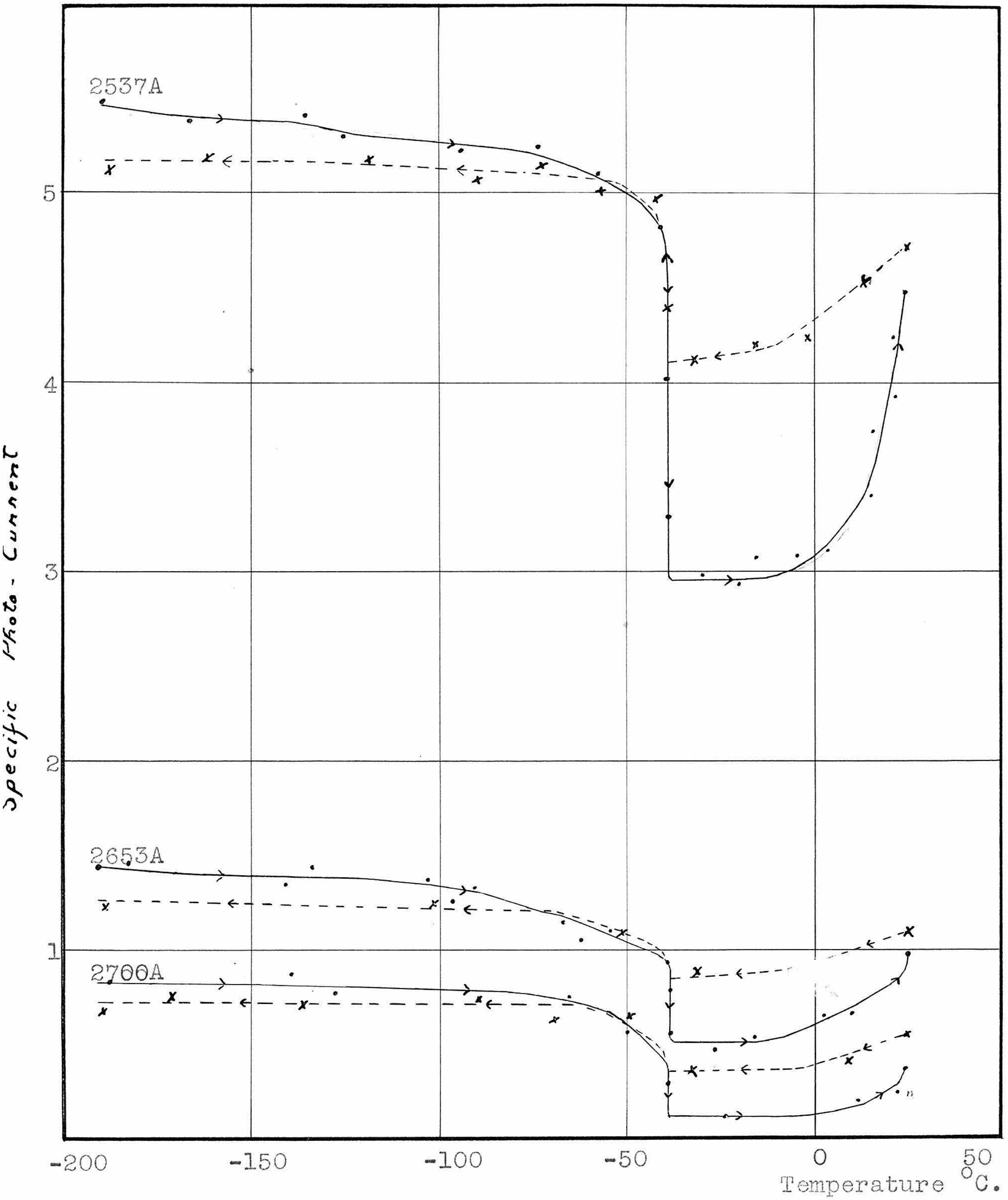
2537A
2653A
2700A
5
4
3
2
1
Specific Photo-Current
-200
-150
-100
-50
0
50
Temperature °C.

Fig. 10

-190° and -125° the sensitivities to 2537A, 2653A and 2700A are about 20%, 40% and 60% higher, respectively, than the corresponding values at room temperature; (b) during melting the sensitivity decreases steadily, the percentage of decrease being about the same for all the lines; (c) as soon as all of the mercury has become liquid, the sensitivity becomes constant, remaining so until the region ca. 0° is reached, where it begins to increase; (d) at room temperature the value is slightly less than the normal value for mercury at this temperature.

The results for decreasing temperature qualitatively are of the same general character as those for increasing temperatures. When the fresh liquid mercury is first cooled the sensitivity decreases somewhat until the freezing point is reached. The decrease is not so large, however, as for correspond-temperatures in the warming-up process. During freezing there is a continuous increase in sensitivity of the same order of magnitude as the decrease in the warming-up process. When all of the mercury has solidified, the sensitivity continues to increase slightly until the region ca.-100° is reached. It then becomes constant at a value somewhat less than the corresponding temperatures for the warming-up process.

The interpretation of Fig. 10 is facilitated by an inspection of the results contained in Figs. 11a, 11b and 11c. These latter curves were obtained by procedures differing in one way or another from the routine one.

Fig. 11a shows the effects on the photo-sensitivity to line 2653A of repeated and prolonged cooling and warming of the mercury cathode. It is to be noted that in this figure the photo-current is plotted as a function of time, and not of temperature. Contamination effects are noticeable, but it is also quite evident that with each change of the mercury from the liquid to the solid phase, and vice versa, there is associated an immediate change of sensitivity.

The results of Fig. 11b were obtained for a case where the cell initially contained no mercury. At the time zero the cell was at room temperature and light of wave length 2537A was incident on the empty iron cup; no deflection of the electrometer was then observable. The cell, still devoid of mercury, was then cooled to -25°; thirty minutes later a current was observable. It was, however, much smaller than

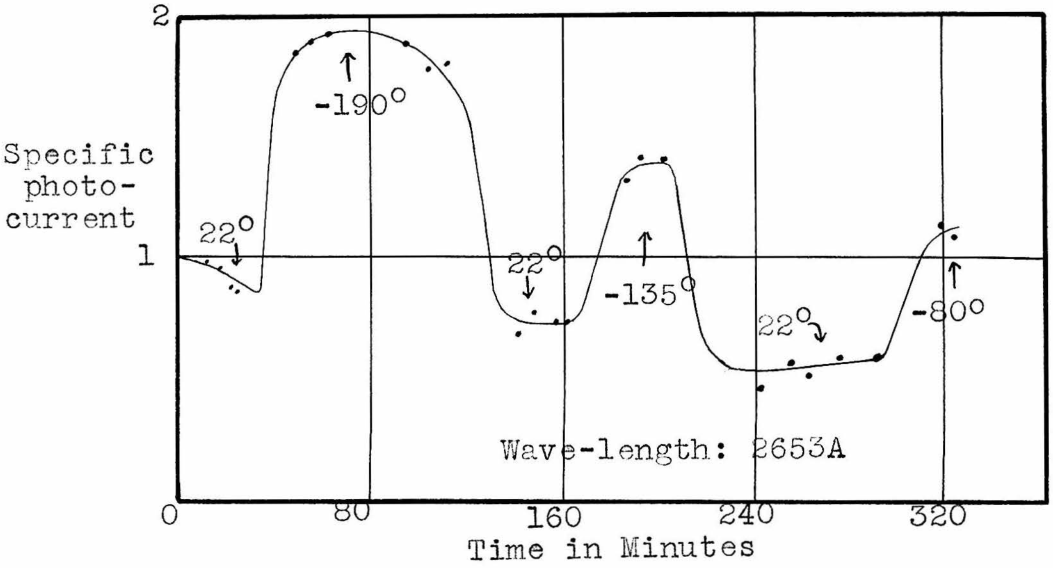

Fig. 11a

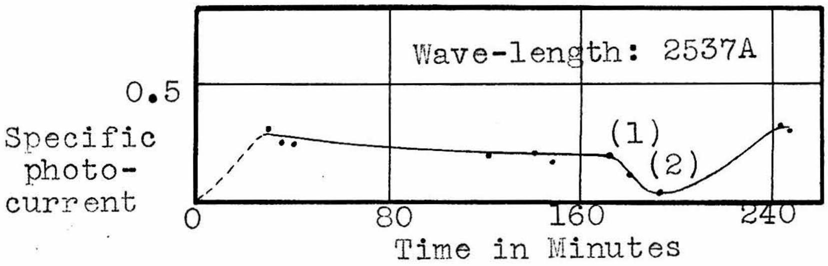

Fig. 11b

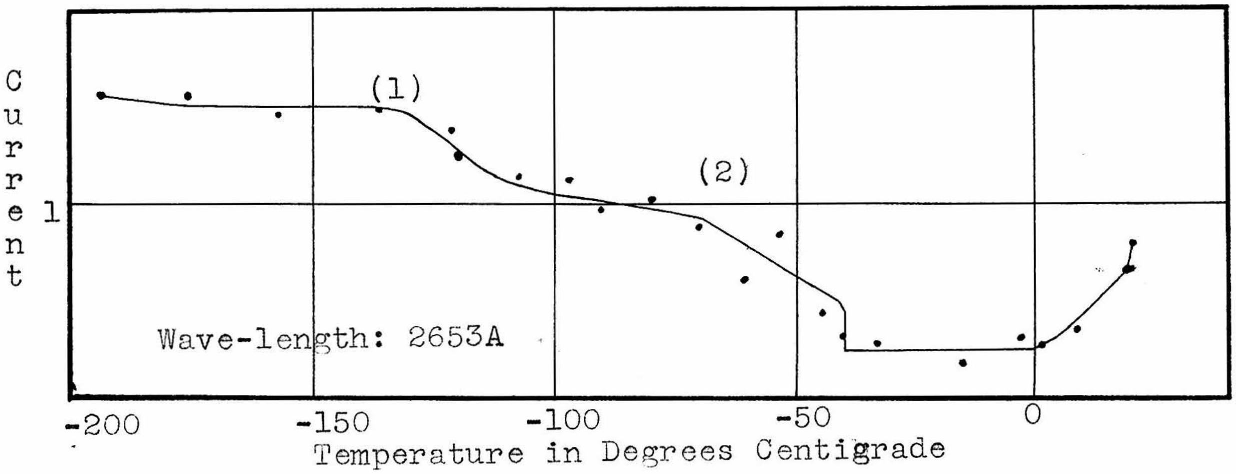

Fig. 11c

the normal value for this line. There is little doubt but that this current came from mercury condensed on the cold iron cathode,--distilled over from the supply of mercury contained in the still and sump. This undoubtedly accounts for a part of the increase in sensitivity occuring when the full cup of mercury is cooled (Fig. 10), For this newly condensed mercury is not only very clean, but probably is initially atomic in structure; the surface which it would form on the solid mercury should be very efficient photo-electrically. At the point marked (1), Fig. 11b, the mercury in the sump adjacent to the photo-cell was heated with a torch; bubbles of gas could be seen escaping from the sump and at the same time the sensitivity of the cathode decreased. Heating the glass walls of the apparatus also lowered the sensitivity. Thus at least a part of the "fatigue" apparent in Fig. 10 can be attributed to adsorbed gases. At the point marked (2), Fig. 11b, the refrigerator was removed from the cell, thus bringing the cathode to room temperature; an increase in the sensitivity resulted. The condensed layer of mercury apparently is quite stable. The action of contaminating substances is seen to be rapid and to be closely associated with changes in temperature.

Unfortunately no further study of this effect was made. The behavior of condensed layers of mercury at very low temperatures should be investigated.

The data for Fig. 11c were obtained and plotted in the same manner as those of Fig. 10, except that *abrupt* increases in the temperature of the mercury cathode and of the cell walls were effected by lowering suddenly the surface of the refrigerating agent surrounding the cell. Such a procedure (points 1 and 2, Fig. 11c) invariably resulted in a lowering of the sensitivity and generally was accompanied by an observable change in the appearance of the mercury surface, usually from a smooth dull gray to a rough metallic appearance. This drop in sensitivity with sudden warming can safely be attributed to a combination of two causes: (1) a transfer of gas from the cell walls to the relatively ~~ly~~ cold mercury; (2) a change in the photo-electric efficiency of the mercury surface due to changes in its structure with sudden changes in temperature. This change in efficiency might be due to a change in the optical absorptivity of the mercury.

SUMMARY OF RESULTS AND CONCLUSIONS

(a) Solid mercury exhibits no variation of photo-sensitivity with temperature in the region -190° to -39°; that is to say, there is no true temperature effect. Slight changes in the slopes of the sensitivity curves, Fig. 10, in the region -125° to -39°, are not reproducible at definite temperatures. They are closely associated with changes in the level of the cooling agent surrounding the cell and with changes in the rates of warming and cooling. Hence they are attributed to the effects of contamination released from or trapped on the cell walls and to changes in the optical absorbtivity of the mercury surface.

(b) No results were obtained which could be attributed to a change in the crystal structure of the solid mercury. Either the structure does not change in the region of temperatures investigated or else the photo-electric effects produced by such a charge in the structure of mercury are too small to be detected by this apparatus.

(c) The threshold for solid mercury is at 2750 25A, as compared with the value 2735 10A for liquid mercury at room temperature. Thus the thresholds for the solid and liquid phases are the same, within the limits of error of the experiment.

(d) The photo-electric sensitivity of solid mercury is higher than that of the liquid. Since there is no accompanying change in threshold, this higher sensitivity is attributed to a change in the photo-electric efficiency of the mercury surface when the metal passes from the liquid to the solid phase. The higher efficiency of the solid mercury may be due to an increase in the optical absorptivity of the surface, for pure mercury has a dull gray appearance when frozen, as contrasted with the well-known specular appearance of the liquid.

It is impossible to say definitely what part of the foregoing increase in sensitivity is due to the condensation of fresh mercury on the frozen surface. From a comparison of Figs. 10 and 11b, it does not seem possible to account for all of the increase in such a way.

(e) Liquid mercury at temperatures between -39° and 0° shows great susceptability to a contamination which lowers the photo-sensitivity. The effects of this contamination begin to disappear when the mercury is heated to a temperature above 0°, and can be eliminated entirely by heating the mercury and cell to a temperature somewhat greater than that of the room.

(f) Three complicating and troublesome factors existed in these experiments. The first of these was the continual condensation of mercury upon the solid mercury cathode. This can be eliminated either by sealing off the photo-cell from the remainder of the apparatus before beginning observations or by placing suitable mechanical valves in the cell outlets.

The second factor, contamination, is not easily eliminated in low-temperature work. The cooled photo-cell acts as a trap. When the cell is cooled suddenly to a low temperature, contamination collects on the cold cell walls, and then transfers to the cold mercury cathode as the cell walls warm up. The most obvious remedy is to employ a cell so designed that the cell walls always are at a lower temperature than the cathode. Placing the liquid air trap very close to the photo-cell also would be an improvement.

The third troublesome factor was the presence of thermo-electric forces. The change from Cell Number One to Cell Number Two was a considerable improvement in this respect, but this troublesome factor can never be entirely eliminated as long as temperature variations are allowed to occure at the point where the anode passes through the Pyrex wall of the cell. Electrostatic effects, occuring in the glass when its temperature is changed, are also a possible source of trouble.

In designing a cell for future work, provision should be made for better thermal contact between the cathode and exterior of the cell. In the case of Cell Number Two is was difficult to bring about rapid changes in the temperature of the cathode because the iron cup was so well insulated thermally from the remainder of the cell. This modification in cell design can be made without difficulty.

APPENDIX I.

A METHOD OF PURIFYING MERCURY FOR PHOTO-ELECTRIC PURPOSES

A METHOD OF PURIFYING MERCURY FOR PHOTO-ELECTRIC PURPOSES

Special precautions are required in the preparation of mercury for use as the active metal in photoelectric experiments. The mercury must not only be free from other metals, but it must be free from grease and other contaminations; hence it must be protected from contamination by rubber and by stopcock grease during the process of distillation.

The author has used with success the following routine in the cleaning of mercury. None of the processes contained in this routine are new, although it has been found to advantage to modify them in certain details. It is considered essential to subject the mercury to all of the processes in the order in which they are named.

STEPS IN THE CLEANING PROCESS

1. Wash the mercury thoroughly in a 10% solution of potassium hydroxide.

2. Shake or mix the mercury for several hours with an equal amount of three-normal nitric acid. This is best accomplished with the aid of the centrifugal rotator, Fig. 12, which is described in detail on a later page.

3. Wash the mercury in distilled water, run it

through a minute pinhole in the apex of a filter paper funnel and finally heat the mercury to 110°C. in a porcelain dish to dry it.

4. Distill the mercury repeatedly by the method of Hulett and Minchin (12), using a somewhat modified form of the still which they describe in their paper. This modified form of still, Fig.13, is described in detail on a later page of this appendix.

5. Pass the mercury through a pinhole in a filter paper funnel, repeating this process until all traces of oxide have disappeared from the surface.

6. Distill the mercury repeatedly in an ordinary still which forms an integral part of the photoelectric apparatus in which the mercury is finally to be used. This process should be carried out in high vacuum and its purpose is to free the mercury from occluded gases. Distillation in a high vacuum will not free the mercury from foreign metals; it is for this latter purpose that step 4 is employed.

DESCRIPTION OF CENTRIFUGAL MIXER

The centrifugal mixer, Fig.12, is easy to construct and it provides a more effective means of treating mercury with nitric acid than does the ordinary "fall" tube, so commonly used in the mercury cleansing process, or than does the ordinary mechanical stirrer.

U.B.Bray made use of the centrifugal mixer in preparing mercury, but he does not describe the device in his paper (18).

The vertical shaft of the mixer consists of a 30 cm piece of 7 mm glass tubing which is closed at the upper end and opened at the lower end. To the lower end of the shaft and at right angles to it is sealed a 10 cm piece of the same kind of tubing, shaped as shown in the photograph, Fig. 12, and drawn out at each end to a 2 mm opening. This cross-piece contains a third opening in its lower center, opposite the point where the shaft and cross-piece are sealed together. The upper end of the shaft is fitted with a piece of a short tubing having an inside diameter slightly greater than the outside diameter of the shaft; this short tube is held in place on the shaft by two perforated corks which fit the shaft tightly. The mixer is clamped in a vertical position in a battery jar containing the mixture of nitric acid and mercury, the lower end of the mixer being placed close to the bottom of the jar. It is necessary to lubricate the portion of the shaft between the two corks with a small amount of vaseline, but if the lower cork fits the shaft tightly, the vaseline will not contaminate the mercury. The mixer should be operated at high speed by means of a

3 a, appendix

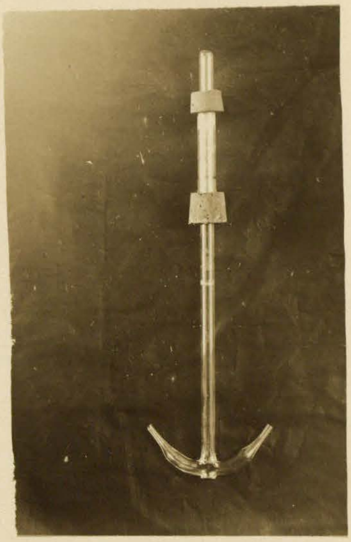

Fig. 12

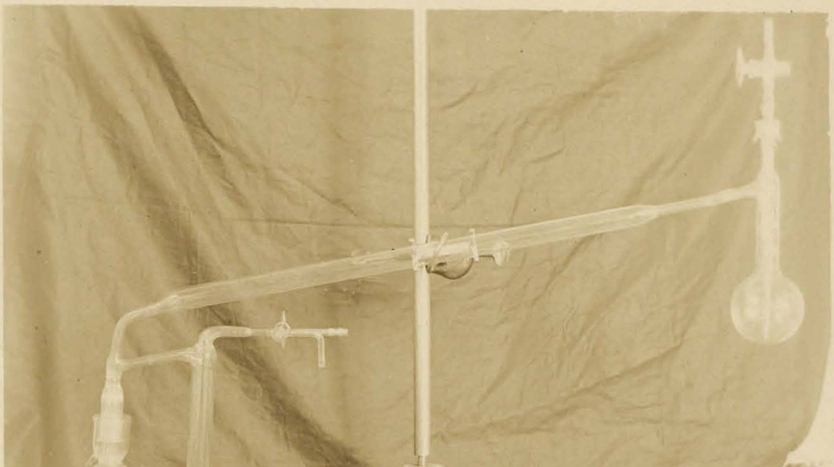

Fig. 13

small motor attached to the shaft with a piece of rubber tubing or a belt.

Sufficient liquid should be placed in the jar to cover the open ends of the mixer. The best results are obtained when the height of the mixer is so adjusted that the mercury and air altermately enter the opening in the center of the cross-piece.

DESCRIPTION OF A MODIFIED FORM OF HULETT AND MINCHIN MERCURY STILL

The still is shown in Fig. 13. It is constructed in the manner described by Hulett and Minchin in their paper (12), except for the following changes:

(a) The long tube which extends down into the distilling flask is held in place in the neck of the flask by a ground glass joint equipped with a mercury seal. Air is admitted to this tube through a stop cock and drying tube, the latter not being shown in the figure. It is suggested that the stopcock be eliminated from the apparatus as a means of controlling the amount of air entering the flask and that it be replaced by a capillary opening, the size of which will have to be determined by trial. If the stopcock is used it may be lubricated with a small amount of graphite, but stopcock grease should be avoided.

If phosphorus pentoxide is used as a drying agent, one should make sure that it does not contain phosphorus and lower oxides, for these impurities are likely to soil the mercury. The phosphorus pentoxide can be purified sufficiently for the present purpose by strongly heating it in a tube, in a current of dry air, before it is placed in the drying tube.

(b) The distance from the spherical portion of the distilling flask to the entrance to the condensing tube should be about 6 cm or more; this reduces the possibility of undistilled mercury being thrown into the condenser.

(c) The receiving bottle is joined to the condensing tube by a ground glass joint, protected by a mercury seal. Such a joint is much more convenient and less fragile than the mercury column of barometric height commonly used at this point. It is, however, more difficult to construct.

(d) The pump or aspirator connection is equipped with a trap and a two-way stopcock . The trap may be cooled with solid carbon dioxide.

It will be seen that this mercury still preserves the essential feature of the Hulett and Minchin apparatus in that it provides for the passage of a current of air through the mercury during the process of distillaation; the function of the air is to oxidize volatile foreign metals and thus remove them completely from the mercury. The still is so constructed that the mercury is protected from such contaminating materials as rubber, stopcock grease, cork, and water vapor.

APPENDIX II

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