THE PHOTOELECTRIC BEHAVIOR OF SOLID AND LIQUID MERCURY

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Abstract

With monochromatic light, the photoelectric threshold wave-length for solid mercury, freshly distilled and frozen in vacuum, was 2750 ± 25A for all temperatures between −190°C and the melting point. For room temperature it was 2735 ± 10A, confirming Kazda's value.

The photoelectric current excited by each of the lines 2537A, 2653A and 2700A was independent of temperature between −190°C and *ca.* −125°C. Between *ca.* −125°C and −39°C there was a gradual small decrease in the current with increasing temperature, but this was not reproducible at definite temperatures and is attributed mostly to contamination and other secondary causes. With the possible exception of this decrease in current, there was no indication of an allotropic change in the mercury between −190°C and the melting point. The photoelectric current for the solid phase was always higher than that for the liquid at room temperature, possibly due to a change in the optical absorptivity of mercury with change in phase. Between −39°C and 0°C the emission curves show so much hysteresis that conclusions regarding this region are impossible.

THE photoelectric threshold for mercury at room temperature has been established at $\lambda_0 = 2735$A by Kazda, Dunn and Hales.[1] Mercury at the melting point was investigated by Pohl and Gudden.[2] They were unable to detect any change in the threshold with melting but terminated their work with the conclusion that mercury is not a suitable metal for studying variations in the photoelectric effect at transition and melting points because of the difficulties inherent in such experiments at low temperatures. Recently, Margarete Grutzmann[3] published a study of the photoelectric emission from mercury at low temperatures. No variation of the total emission with temperature was found and there was no change in the total emission at the melting point. Since monochromatic light was not used, it is impossible to interpret these results or to establish the behavior of the threshold.

The purposes of the present work with mercury were: (1) to find the effects of temperature and of changes in the state of aggregation on the photoelectric threshold and on the current excited by incident monochromatic light; (2) to check independently the value of the threshold at room temperature; (3) to seek evidence of a photoelectric nature regarding an allotropic change in mercury in the region between −190° C and the melting point. McKeehan and Cioffi[4] determined the crystal structure of mercury

[1] C. B. Kazda, Phys. Rev. **26**, 643 (1925); H. K. Dunn, Phys. Rev. **29**, 693 (1927); W. B. Hales, Phys. Rev. **32**, 950 (1928).

[2] Pohl and Gudden did not publish. This information was communicated to me by Dr. A. Goetz.

[3] M. Grutzmann, Ann. d. Physik **1**, 49 (1929). A comprehensive bibliography accompanies this paper.

[4] McKeehan and Cioffi, Phys. Rev. **19**, 444 (1922).

at $-115°$ C and Alsen and Aminoff[5] determined the structure at $-78°$ C. The two results are very different and thus point to the existence of an allotropic modification of the mercury occurring somewhere between $-115°$ C and $-78°$ C.[6] On the other hand, Lark-Horovitz[7] has recently found that the crystal structure of mercury at the temperature of liquid air is identical with that at the temperature of a carbon dioxid-alcohol mixture.

The apparatus for the present work, Fig. 1, was made of Pyrex glass and had no cemented joints or stopcocks in the high-vacuum system. Light from a mercury arc, which had been carefully calibrated[8] and which was operated with constant voltage, current and temperature, passed through a Hilger quartz monochromator and a quartz lens into the quartz window of the photoelectric cell, and then through a slit in the anode onto the bottom of the cell. The anode was a circular disk of tungsten 3 cm in diameter, welded with nickel to a heavy tungsten wire which lead out through a horizontal tube 12 cm long to a Dolazalek electrometer of sensitivity 1100 mm

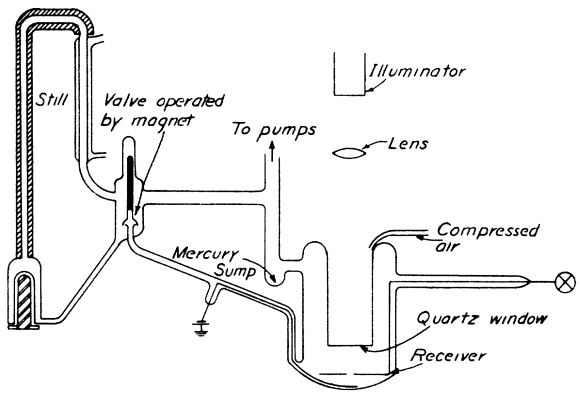

Fig. 1. Diagram of apparatus.

per volt at 1.5 m scale distance. The cell was shielded electrostatically by covering its outside walls with a paste made of powdered graphite, water, and a little water glass. When the cell was baked the graphite formed a hard conducting layer. Water glass, when used sparingly, apparently will not weaken Pyrex appreciably, for the cell was used for two months without breakage.

The mercury used as the cathode of the cell was cleaned and distilled by a special method[9] and was then placed in the still, Fig. 1, where it was distilled repeatedly in high vacuum to remove occluded gases. Some of the mercury was then allowed to pass through a magnetically operated valve, Fig. 1, into the bottom of the cell, where it rested on the glass, but was in

[5] Alsen and Aminoff, Geol. Foren. i. Stockholm Forh. 124 (1922).

[6] Ewald and Hermann, Zeits. f. Krist. **65,** parts 1–3, appendix (1927); International Critical Tables, **1,** 340.

[7] K. Lark-Horovitz, Phys. Rev. **33,** 121 (1929).

[8] C. B. Kazda, Phys. Rev. **26,** 645 (1925).

[9] D. Roller, J. O. S. A. **18,** 537 (1929).

contact with a tungsten wire kept usually at a potential of 20 volts negative to ground.

The cooling of the mercury was accomplished variously with liquid air, liquid air and alcohol, solid carbon dioxide, and solid carbon dioxide and ether, contained in a specially designed Dewar flask which surrounded the cell up, to a point 7 cm above the surface of the mercury cathode. Temperatures were measured with a constantan-steel thermocouple, enclosed in a glass tube and immersed in the mercury. To retard the collection of moisture on the cold cell, a current of washed and dried air was played continuously on the window and walls. The points where the tungsten leads emerged from the cell were kept dry by means of small heating coils and drying materials. Surrounding the cell was a double-walled galvanized iron box, lined with asbestos, which helped to keep out moisture and which also served as an oven for baking the cell and as an additional electrostatic shield.

With the cell of Fig. 1 the threshold for mercury at room temperature was found to be at 2735 ± 10A, in agreement with the results of previous workers.[10] This constitutes an independent check of the previous work, both because the mercury was here in contact with glass and tungsten, rather

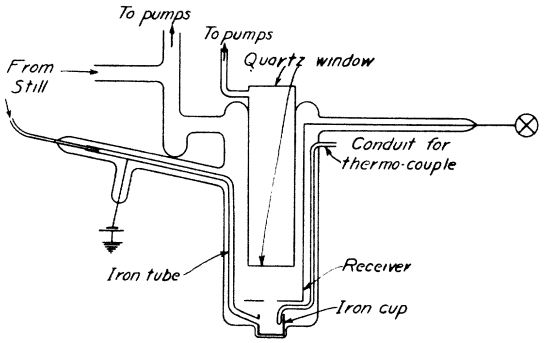

Fig. 2. Diagram of modified apparatus.

than iron, and because the cell involved relatively few metal parts and probably was more thoroughly outgassed than the cells previously used.

When it was attempted to use this cell for low temperature work several defects in its design became apparent and this led to the construction of a new cell, Fig. 2, which differed from the old one in the following respects. (a) A second quartz window was cemented to the cell at a point considerably above the region to be cooled, the space between the two windows being evacuated. This gave improved thermal insulation and also made it possible to dispense with the current of air on the cell. Compressed air usually contains oil which forms a film on the window; no simple way could be found for removing all the oil from the air. (b) The anode, including the lead through the glass wall of the cell, was cut out of a single sheet of tungsten. In the old cell, the anode consisted of a tungsten sheet welded to tungsten wire and it was the seat of thermoelectric forces which produced erratic effects during times that the temperature of the cell was changing. (c) An iron cup 2.5 cm in diameter served as a container for the mercury cathode, the size of this cup being such that light fell only on the central unstrained part of the frozen

[10] Reference 1.

mercury. The mercury was admitted to the cup through an iron tube, so arranged that it did not need to pass through the glass wall of the cell. In the old cell the mercury ran in over the glass, resulting in the formation of electrostatic charges which would persist for as much as an hour. (d) The mercury pump attached to the cell was enlarged so that it could be immersed in liquid air, thus retarding the condensation of mercury vapor on the surface of the solid mercury cathode. Preliminary experiments had shown that without this protection enough mercury condensed on the surface of the empty iron cup, when the latter was cooled, to produce an appreciable photoelectric current. Experiments made very recently at the University of Oklahoma by Mr. Carl Woodward and the writer indicate that a thin film of frozen mercury deposited on iron has both a high photoelectric sensitivity and a threshold wave-length longer than 2735A. In view of these results, it might be advisable to seal off the photoelectric cell from the pumps and mercury still before attempting to determine the threshold of solid mercury.

In order to determine the thresholds at various temperatures, measurements were made of the photoelectric current at a particular temperature as a function of wave-length. Thresholds were then determined in the usual way by plotting the current excited by unit intensity of the incident light as a function of wave-length.[11] In the region $-190°$ to the melting point, the threshold was established at 2750 ± 25A, independently of the temperature. Thus, within the experimental error, the threshold for solid mercury is the same as that for liquid mercury at room temperature. When the solid mercury was held at low temperatures for times exceeding about one hour, the threshold began to shift slowly to shorter wave-lengths. There was ample evidence that this shift was due to contamination.

Measurements were also made of the photoelectric current for a given line as a function of temperature. Results typical of sixty curves made for the lines 2537A, 2653A, and 2700 A are shown in Fig. 3. The arrows indicate the direction of temperature variation. The time required to obtain data for a given curve varied between 30 minutes and 12 hours, depending upon the method of cooling and the number of observations made.

Fig. 3 shows that the sensitivity of the mercury to monochromatic light was practically independent of temperature in the region $-190°$ to *ca.* $-125°$. Between the latter temperature and the melting point, $-39°$ C, slight changes occur in the slopes of the sensitivity curves but these could not be reproduced at definite temperatures. They were found to be associated closely with changes in the level of the cooling agent surrounding the cell and with abrupt changes in the rate of warming and cooling. Experiments showed that contamination released from the walls of the cell lowered the sensitivity of the mercury. Abrupt changes in temperature had a marked effect on the appearance of the solid mercury surface, particularly when the mercury was near the melting point; thus it is very likely that such abrupt changes of temperature also affected the photoelectric efficiency of the mercury surface.

Nothing was observed in the region between $-190°$ and $-39°$ C that could be attributed to an allotropic change in the mercury. This excepts

[11] R. A. Millikan, Phys. Rev. **7**, 380 (1916).

the slight decreases in sensitivity which always accompanied rises in temperature and which have been at least partly accounted for in other ways.

During melting and freezing the sensitivity of the mercury changed rapidly. In the region between $-39°$ and $0°$ C the liquid mercury showed great susceptibility to some unknown contamination which lowered the sensitivity. The curves, Fig. 3, show so much hysteresis in this region that no conclusions can be made as to the effect of temperature on the liquid mercury. The contamination was of such a kind that it could be eliminated immediately from the mercury surface by heating the cell a few degrees above room temperature.

It is to be noted that the sensitivity of the solid mercury always was higher than that of the liquid at room temperature. Since the thresholds

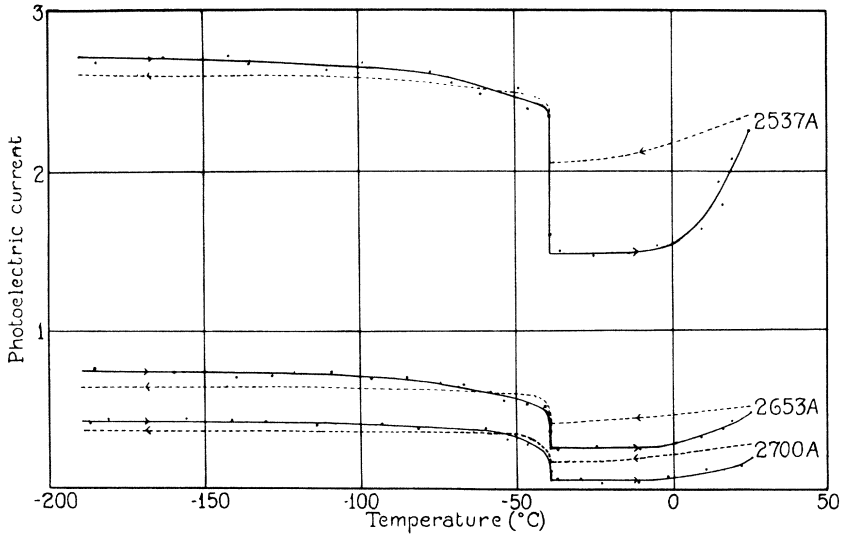

Fig. 3. Photoelectric current for lines 2537A, 2653A and 2700A as a function of temperature.

were found to be the same in the two cases, the higher sensitivity of the solid must be attributed to a change in the photoelectric efficiency of the mercury surface with change of state. This change in efficiency may be due to a change in the optical reflectivitity of mercury with change of state. No exact information is at present available regarding the reflectivity of a very pure solid mercury surface formed in high vacuum although experiments are in progress. Haak and Sissingh[12] found no change in the optical constants of mercury either on freezing or in subsequent cooling down to $-80°$ C, but the mercury surfaces used by them contained adsorbed layers of air.

This work was done in 1928 at the Norman Bridge Laboratory of Physics, California Institute.

It is a pleasure to acknowledge my indebtedness to Professor Millikan whose interest and guidance prompted the choice of subject and made the work possible.

[12] Haak and Sissingh, K. Akad. Amsterdam **21**, 678 (1919).