SOME PHOTOELECTRIC PROPERTIES OF MERCURY FILMS

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Abstract

Films of very pure mercury were deposited slowly in a high vacuum on an oxidized iron plate maintained at liquid air temperature. As each film increased in thickness, the photoelectric current excited by each of the mercury arc lines 2537A, 2653A and 2700A increased from zero to a maximum value and then decreased to a final constant value. In each case the threshold wave-length at the time of maximum sensitivity was *ca.* 2750A. Its final value, that for a thick layer of mercury, was 2730 ± 15A; this did not change even when the mercury was allowed to melt, thus confirming a previous conclusion that the theshold wave-lengths for solid and liquid mercury are the same. There was no indication of a large shift in threshold wave-length at any time during the formation of the films.

THE photoelectric properties of thin films of various metals have been the subject of study for two decades[1] but determinations of the photoelectric threshold wave-lengths of films of atomic dimensions deposited slowly in a high vacuum are comparatively recent and have been confined largely to the alkali metals.[2,3,4] The characteristic feature of such an alkali metal film is that as it accumulates, the photoelectric threshold wave-length moves from the blue end of the spectrum toward the red, reaches an extreme value which for the majority of the alkali metals is in the infrared, and then recedes again to the final value characteristic of the metal in bulk.

In the present work the object has been to observe the behavior of the photoelectric current and threshold wave-length for films of mercury slowly deposited on iron in a high vacuum. Most of the photoelectric work with mercury has been confined to the liquid[5] and solid[6,7] in bulk, an exception being the work of McLennan, Hunter and McLeod[8] on the photoelectric effect of metals at the transition temperatures where they exhibit the property of superconductivity. Although the work with mercury was finally abandoned because of the unsuitableness of mercury films for the purpose of the investigation, preliminary experiments showed that the total photoelectric current from mercury deposited on glass was greater with a thin film than with a

[1] Gudden, Lichtelektrische Erscheinungen, Julius Springer (1928), Chap. 5, is perhaps the best recent summary of this work.

[2] Ives, Astrophys. J. **60,** 209 (1924).

[3] Ives and Olpin, Phys. Rev. **34,** 117 (1929).

[4] Campbell, Phil. Mag. **6,** 633 (1928); **8,** 557 (1929).

[5] Kazda, Phys. Rev. **26,** 643 (1925); Dunn, Phys. Rev. **29,** 693 (1927); Hales, Phys. Rev. **32,** 950 (1928); Roller, Phys. Rev. **32,** 323 (1928).

[6] Grutzmann, Ann. d. Physik **1,** 49 (1929).

[7] Roller, Phys. Rev. **36,** 738 (1920).

[8] McLennan, Hunter and McLeod, Roy. Soc. Canada, Trans. **24,** Sec. 3, 3 (1930).

thick one. Monochromatic radiation was not used in this work and no attempt was made to determine threshold wave-lengths.

Apparatus

The photoelectric cell was a Pyrex glass tube 3.7 cm in diameter, to the upper end of which was sealed a graded quartz-Pyrex seal containing a quartz window and to the lower end a plane Pyrex plate which formed the bottom of the cell (Fig. 1). In contact with the latter was a 3.3 cm disk of oxidized Swedish wrought iron upon which the film of mercury was allowed to deposit. This plate was maintained at 30 volts negative to ground, a potential found to be sufficient for producing a saturated photoelectric current with this cell. The anode consisted of a network of fine tungsten wire supported on a horizontal loop of 0.8 mm tungsten wire, an opening in the network being provided for illumination of the cathode. The anode was not in contact with any part of the cell except at the sealing-in point. The cell was shielded electro-

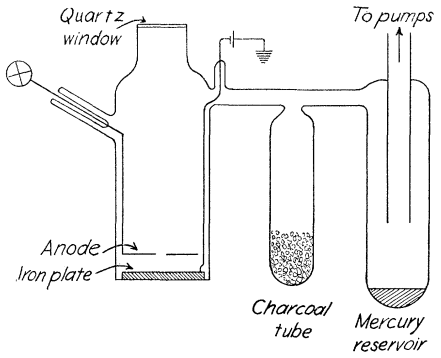

Fig. 1. Diagram of photoelectric cell.

statically by a coat of tin foil on the outside walls. The exhaust tube of the cell, to which was attached a liquid air tube containing cocoanut charcoal, was connected through a reservoir for mercury, a second liquid air trap and a mercury "cut-off" to a two-stage water-cooled mercury diffusion pump backed by a Cenco Hyvac fore-pump. The vacuum system included a McLeod gauge and a still for repeated distillation of the mercury in high vacuum. The usual precautions were taken to exclude wax and grease vapors. There was one stopcock, next to the fore-pump, but air was never admitted to the system through it.

The source of radiation was a General Electric Vapor Lamp Company horizontal-type 110-volt d.c. quartz mercury arc, enclosed in an asbestos-board housing and operated at 65 volts and 3.7 amperes. This was used in connection with a Leiss quartz monochromator and a pair of quartz lenses which formed an image of the slit 1 cm in length on the cathode of the cell. Intensity measurements of the radiation were made by means of a Burt vacuum thermocouple connected to a Leeds and Northrup high-sensitivity D'Arsonval galvanometer. Photoelectric currents were measured by a Dole-

zalek electrometer, the rate-of-charge method being used. The sensitivity of the electrometer was 2000 mm per volt at 3 m scale distance.

The foregoing description applies to the apparatus in its final form, as it was designed and completely reconstructed after extensive preliminary experiments. In the original apparatus, the metal surface in the cell, on which the mercury films were deposited, consisted of a horizontal iron disk 2.9 cm in diameter, mounted on a vertical tungsten rod sealed through the bottom of the cell. To the lower end of this rod was attached a small aluminum cylinder which could be immersed in liquid air when it was desired to cool the cathode. It was found, however, that a cathode of this type could not be cooled uniformly and that its temperature, when it was cooled, was below that of any other part of the cell, thus increasing the chance of contamination collecting on the deposited mercury. The original apparatus did not include a charcoal tube and all the preliminary observations were made with the cell attached to the pumps.

Procedure and Results

In the work with the improved apparatus, when the vacuum was as good as could be read on the McLeod gauge, the cell, charcoal tube and empty mercury reservoir were baked in ovens for 170 hours at 450, 550 and 550 degrees C, respectively, and the remainder of the glass system was heated with a torch. The highly-purified mercury[9] contained in the still was in the meantime distilled repeatedly in the high vacuum to remove occluded gases and then, with the temperature of the charcoal tube lowered to 350°C, some of this mercury was made to collect in the reservoir near the cell. The cell, charcoal tube, and reservoir were then sealed off as a unit from the remainder of the apparatus.

With the charcoal tube already in liquid air, the mercury in the reservoir was frozen by means of liquid air in order to prevent mercury from distilling over into the cell prematurely. The photoelectric cell was then immersed in liquid air up to a point on the cell walls about 2 cm above the surface of the iron cathode. As soon as the electrometer became steady, which usually required about five minutes, the liquid air was removed from the reservoir but not from the charcoal tube. About 30 minutes later the mercury depositing on the iron cathode began to exhibit a photoelectric sensitivity to the line 2537A and in approximately 110 minutes this sensitivity reached a maximum value.

Attempts had previously been made to make measurements without having a liquid air tube between the cell and reservoir and without having the mercury in the reservoir initially frozen; but the mercury then accumulated on the cathode so rapidly that the maximum sensitivity was reached within a few minutes after cooling the cell, at a time when the electrometer was still very erratic.

Measurements were made of the photoelectric current for each of the monochromator drum-settings 2537, 2653, 2700, 2752, 2804 and 2900A and

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

for settings midway between these lines. The electrometer deflections for the drum-settings 2752, 2804 and an intermediate setting were always small and practically equal in magnitude. In the case of the lines 2537, 2653 and 2700A the results were like that shown in Fig. 2, in which the current is plotted as a function of the time elapsing after the removal of the liquid air from the reservoir.

Thresholds wave-lengths for various stages in the formation of the film were determined in the usual way by plotting the current per unit intensity of the exciting radiation as a function of wave-length. The values of these thresholds were found to be always between 2720A and 2750A, regardless of the thickness of the film. Thus they agree, within the experimental error, with the threshold values for mercury in bulk, namely 2735 ± 10A for the

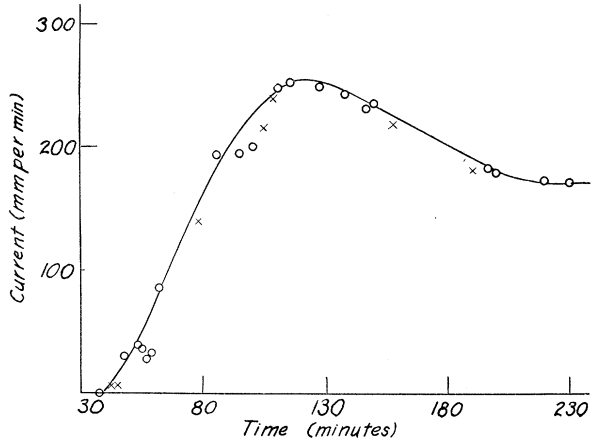

Fig. 2. Photoelectric current for the line 2653A vs. time of deposit.

liquid at room temperature[5] and 2750 ± 25 for the solid between $-190°$ C and the melting point.[7]

For any given film there was usually a progressive change in the threshold from shorter to longer wave-lengths as the time of deposit approached that corresponding to a maximum photoelectric current. At the latter time the threshold was always close to 2750A. Afterwards, while the photoelectric current was decreasing (Fig. 2), the threshold always returned to 2730 ± 15A. This final value, which was the threshold for a thick layer of mercury, did not change even when the mercury was made to melt by removing the liquid air from the cell. This confirms a previous conclusion[7] that the thresholds for solid and liquid mercury are the same.

During all of this work there was very little evidence of effects that could be attributed to contamination. Of the various contaminating substances that were likely to have been present in the cell, oxygen is believed to be the only one that will alter the long wave limit of mercury[10] and Poole[11] has con-

[10] Hales, Phys. Rev. **32,** 950 (1928).

[11] Poole, Thesis, California Institute of Technology (1927).

cluded that even oxygen is not effective unless it is in the presence of water vapor or has been exposed for some time to ultraviolet light. In view of this freedom of the cell from contamination, it would appear that the excursion of the threshold toward longer wave-lengths and the subsequent return to shorter wave-lengths as the film builds up is a true effect although it evidently is an exceedingly small one. In the case of very thin films of the alkali metals the thresholds are of the order of magnitude of 1000A farther toward the red end of the spectrum than are the thresholds for the metal in bulk.[2,3,4]

Experiments were also made with mercury condensed on the iron plate at a temperature above the freezing-point of mercury. The cell was cooled with ice and the deposit was accelerated by warming slightly the mercury reservoir with a small heating coil. At all times during the deposition of the mercury, the threshold wave-length was 2730 ± 10, which is practically the same as that for the liquid in bulk. The photoelectric current, on the other hand, increased steadily until it reached a maximum value but this was not followed by a decrease of the type observed with films deposited at the temperature of liquid air. At the end of an hour the deposit could be seen to consist of minute globules of mercury. Observations over a period of seven hours showed that these globules increased in number and slowly grew in size until they came into contact with one another and united. The unions were accompanied by slight decreases in the photoelectric current, probably due to decreases in the area of photoelectrically active metal exposed to the radiation.

In previous experiments made by one of us,[7] it was found that the photoelectric sensitivity of solid mercury in bulk was always higher than that of the liquid and this was attributed to a change in the photoelectric efficiency with change of state, due possibly to a change in the optical reflectivity. Recent experiments in this laboratory by W. Webb[12] show that when mercury is alternately frozen and melted in vacuum in such a way as to form a specular surface and under conditions unfavorable for the condensation of mercury vapor on the solid surface, then the monochromatic reflectivities for the solid and the liquid are the same for all the strong lines in the spectral region 4558–2537A. Ordinarily, however, frozen mercury presents an irregular surface that has the appearance of being a better absorber of radiation than the liquid. Whether this apparent increase in the "blackness" of the surface would account for the higher efficiency of the solid or whether there is also a change in the quantum equivalent of mercury with freezing would be difficult to determine.

[12] Not yet published.