

## PHYSICAL SCIENCES

## I. THE PHOTOELECTRIC SENSITIVITY OF THIN FILMS OF SOLID MERCURY

CARL S. WOODWARD AND DUANE ROLLER  
University of Oklahoma

In the region of temperatures  $-125^{\circ}\text{C}$ . to  $-190^{\circ}\text{C}$ . solid mercury shows an increase in photoelectric sensitivity and a shift of threshold toward longer wave-lengths.<sup>1</sup> Of the several possible explanations of this effect, one is that the mercury vapor in the photoelectric cell condenses on the cold mercury cathode, forming a very thin film of mercury. Although heretofore not observed for mercury, it is known that certain other metals, notably those of the alkali group, exhibit both a high sensitivity and a shift of threshold wave-length toward the red when in the form of thin film.<sup>2</sup> The present work represents the first of a series of experiments to determine whether thin films of mercury possess similar properties.

The photoelectric cell used in this work was of special design (Fig. 1). The cathode on which the mercury film was to be deposited consisted of a horizontal iron plate 2.9 c. m. in diameter. Iron was used because it has a larger work function than mercury and is not attached chemically by the latter metal. The iron cathode was mounted on a vertical tungsten rod which was sealed through the Pyrex bottom of the cell, and to the outside end of which was attached a larger aluminum rod for increasing the cooling area of the cathode. The cathode was maintained at a potential of 25 volts negative to ground. The anode of the cell consisted of a horizontal circular loop of 0.8 mm. tungsten wire, distant 1.5 c. m. from the cathode; this tungsten wire passed out of the cell through a horizontal tube 7 c. m. in length and was connected to a shielded copper wire leading to a Dolezalek electrometer. The walls of the cell and of the remainder of the system were of Pyrex, the radiation being admitted to the cell through a quartz window attached to the cell by means of a graded seal. The cell and electrometer were shielded from electrostatic disturbances.

A mercury still was connected to the cell through a water-cooled tube, this still being so designed that the mercury to be used for forming the thin films could be repeatedly distilled in high vacuum to remove occluded gases. The remainder of the apparatus, including the evacuation system and source of monochromatic radiation, and the method of operation were substantially the same as in former work with mercury.<sup>1</sup> There were no stop-cocks or cemented joints in the high-vacuum system. The cell was baked in an oven during the initial stages of evacuation. The sensitivity of the electrometer was about 700 mm. per volt for a scale distance of 3 meters. The mercury arc lamp was operated at ca. 80 volts and 3.5 amperes, the source of current being a 110-volt d. c. generator; the variations in voltage of this source amounted to as much as 3 volts. Monochromatic radiation was obtained by means of a Leiss quartz monochromator.

The initial attempt to condense mercury on the cathode of the cell failed because of the great length of the vapor path between the still and cell. To remedy this, a sump (Fig. 1) was attached to the system close to the cell, and the mercury was first distilled over into the sump.

Before proceeding with the work on frozen films, an attempt was made to deposit a mercury film on the cathode at a temperature above the melt-

<sup>1</sup>Robinson, *Phil. Mag.* 25, 116 (1913); Ives, *Astrophys. J.*, 60, 208 (1924) and 64, 123 (1926); Ives and Olpin, *Phys. Rev.* 34, 117 (1932); etc.  
<sup>2</sup>Roller and Woodward, *Okl. Acad. Sci. Proc.* 10, 122 (1935); Roller, *Phys. Rev.* 36, 734 (1936).

ing point of mercury and to observe its photoelectric properties. The mercury vapor was driven from the sump to the cathode by slightly warming the sump by means of an electric heater, and at the same time cooling the cathode with ice applied to the tungsten lead. Eight sets of photoelectric readings were taken with these liquid deposits as the photoelectrically active surface, but there was no indication of a shift of the threshold from the established value for mercury, namely 2735A, during the time that the deposits were forming on the cathode. An inspection of the deposit with a simple microscope showed that it consisted of minute globules of mercury which were continually uniting with one another as the globules increased in size. One could actually watch the globules unite and observe simultaneously a decrease in the electrometer reading, due presumably to the decrease in the area exposed to the radiation and also possibly to electrostatic effects. In other words, the liquid mercury apparently never formed true films.

To obtain films at temperatures below the freezing point of mercury, the lead to the cathode was immersed in liquid air, the only easily procurable refrigerant having a low enough temperature. The temperature gradient between the sump and cathode thus being very large, the solid film began to form during the first few moments of cooling, which is undesirable, since this is the time when the electrometer is always the most erratic. Although effects due to leakage over the cooled walls of the cell could be reduced by using guard-rings and drying agents, it was found impossible at the time to eliminate erratic effects due to temperature changes in the electrometer circuit. In continuing this work, a method for cooling the cell must be devised which will afford better temperature control and a slower formation of the film on the cathode. By suitably choosing the metals employed in the cell and electrometer circuit, it may be possible to eliminate part of the erratic behavior of the electrometer during the cooling of the cell.

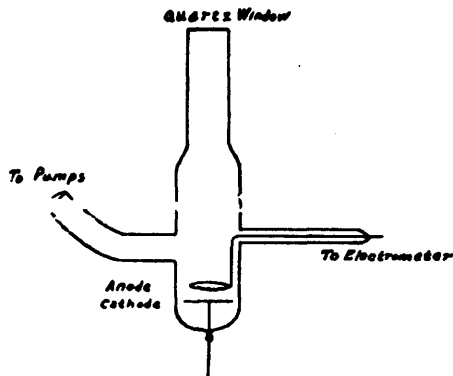
Because of the aforementioned complications, it was difficult to obtain consistent data for the photoelectric sensitivity of the films during their early formation. The data in Table I are typical of all the results obtained with frozen films. The time of observation in each case was measured from the moment when the liquid air was applied to the cathode, the relative times in a given set of observations being considered to be an indication of

TABLE I.—Photoelectric Sensitivity of Mercury Films of Varying Thickness, for Wave-lengths Longer than the Normal Threshold, 2735A.

Trial	$n\lambda$ in Angstroms	Age of films, minutes	ELECTROMETER DE- FLECTIONS, mm.		Photo- electric current, mm./min.
			1st min.	2nd min.	
1	2893	1	- 4	4	0
		3	49	12	37
		5	9	6	3
		7	4	2	2
2	2803	1	15	1	14
		3	5	- 3	18
		5	1	- 5	6
	2537	35	580	30	550
	2652	38	170	20	150
3	2803	1	47	3	44
		3	1	- 2	3

the relative thicknesses of the film. Although no threshold determinations were made, the data in Table I are for wave-lengths longer than the normal threshold of mercury, 2735A, and therefore indicate a shift of threshold toward the red. In one case, trial 1, the sensitivity to the line 2893A first increased and then decreased with time, a result which is in agreement qualitatively with work on thin films of other metals.

Figure 1.—The Photoelectric Cell.



Legend for Figure to Accompany Woodward-Roller Photoelectric Sensitivity of Thin Films of Mercury: