



EFFECT OF TEMPERATURE ON THE PHOTOELECTRIC BEHAVIOR OF SOLID AND LIQUID MERCURY

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The purposes of this 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.

The apparatus, 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 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 into 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 led out through a horizontal tube 12 cm long to a Dolzalek electrometer of sensitivity 1100 mm 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.

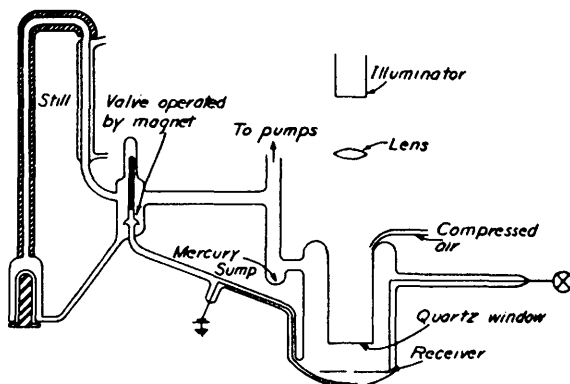


Fig. 1. Diagram of Apparatus.

The mercury used as the cathode of the cell was cleaned and distilled by a special method¹ 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 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 7cm 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.

The threshold for mercury at room temperature was found to be at $2735 \pm 10A$, in agreement with the results of previous workers.² This constitutes an independent check of the previous work, both because the mercury was here in contact with glass and tungsten, rather 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

¹D. Roller, *J. O. S. A.* 18, 537 (1929).

²C. B. Kazda, *Phys. Rev.* 26, 643 (1925); H. K. Dunn, *Phys. Rev.* 29, 693 (1927); W. B. Hales, *Phys. Rev.* 32, 950 (1928).

of a new cell 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 and 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 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.

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. In the region -190° to the melting point, the threshold was established at $2750 \pm 25 \text{ \AA}$, 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 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 2700A are shown in Fig. 2. 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. 2 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 temperatures 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 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 the slight decrease 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. 2, shows 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

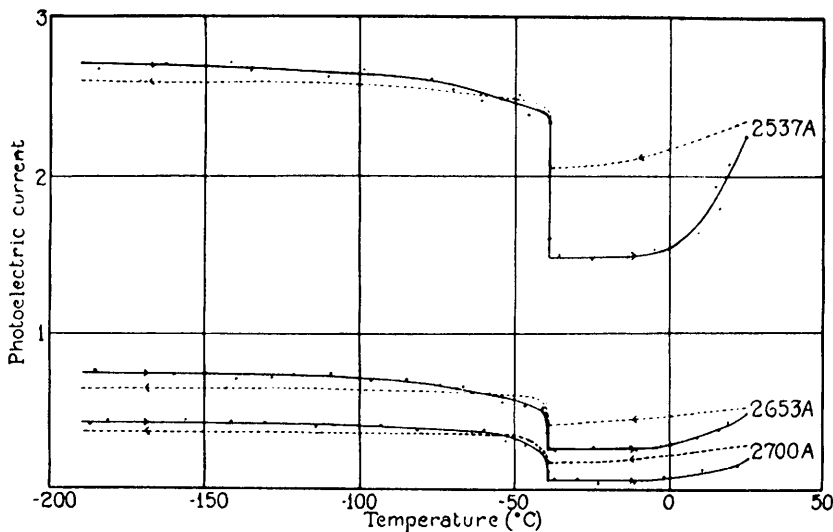


Fig. 2. Photoelectric current for lines 2537A, 2653A and 2700A as a function of temperature.

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 reflectivity of mercury with a 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.

Experiments are in progress on the photoelectric behavior of very thin films of solid mercury.