THE PERSISTENCE OF THE RADIATION EXCITED IN MERCURY VAPOR

By Lucy J. Hayner

Abstract

A photographic method was used. Light from an intermittent mercury arc passed through a quartz cell containing Hg vapor at 40° to 100°C, and then together with the excited radiation through a hole in a rotating sector into a spectrograph. The sector was mounted on the shaft of the commutator which operated the arc. Thus for λ2537 a trace was obtained on the plate, whose length depended on the time of persistence of the radiation, the time scale being determined by the speed of rotation. Measurements of the blackening showed that the decay was exponential. The time to decrease to intensity $1/e$ came out 4.0×10^{-5} and 6.8×10^{-5} sec. for cells of length 1.6 and 3.2 cm respectiyely. For the arc alone in a tube of 0.9 cm radius the constant was 0.6×10^{-5} sec , while for the arc at the center of a bulb of 3 cm radius the constant was 5.5×10^{-5} sec, The decay was found to be independent of the vapor pressure from .006 to .27 mm for the cell and from .05 to 1.7 mm for the bulb. No persistence was observed when the cell did not contain distilling mercury or when it was sealed off from the pump. Fresh mercury seems to be necessary and also the absence of impurity. It is interesting to note that the time constants are of the order of magnitude of the times required for atoms at the temperatures involved to go without impact from the center to the wall of the cell.

In a recent series of experiments Webb[1] studied by an electrical method the life of the resonance radiation λ2537 in mercury vapor. The radiation was excited by electron impacts under voltage sufficient to lift the valence electron to the $2p_2$ orbit. His results gave pressure and dimension relations not in agreement with those required by the "imprisonment theory" of repeated absorption and re-emission. Accordingly a metastable state for $2p$ was postulated. In this case the life of the radiation in the apparatus must depend largely upon the motion of the excited atoms. Approximate calculations based on this assumption agreed well with the experimental facts. The present paper describes experiments made to determine the persistence of λ2537 excited by resonance absorption in a vessel containing mercury vapor, a case in which the process of absorption and re-emission must play an important part. The rate of decay of this radiation excited by striking an arc was also measured.

[1] H. W. Webb, Phys. Rev. **24**, 113 (1924).

Method

A photographic method was used. This had a great advantage over the electrical method in that the spectral lines could be studied separately. It had the disadvantage, however, that a large amount of radiation was necessary. The resonance line λ2537 could not be produced below the ionization potential with sufficient intensity and it was therefore necessary to use the radiation λ2537 from an arc for the excitation of the resonance radiation. Thus the complex arc spectrum was always present during the excitation.

The apparatus is shown schematically in Fig. 1. The source *A* was a hot cathode arc in a quartz flask. For the study of the fluorescent radiation excited in a separate vessel, an evacuated quartz cell *B*

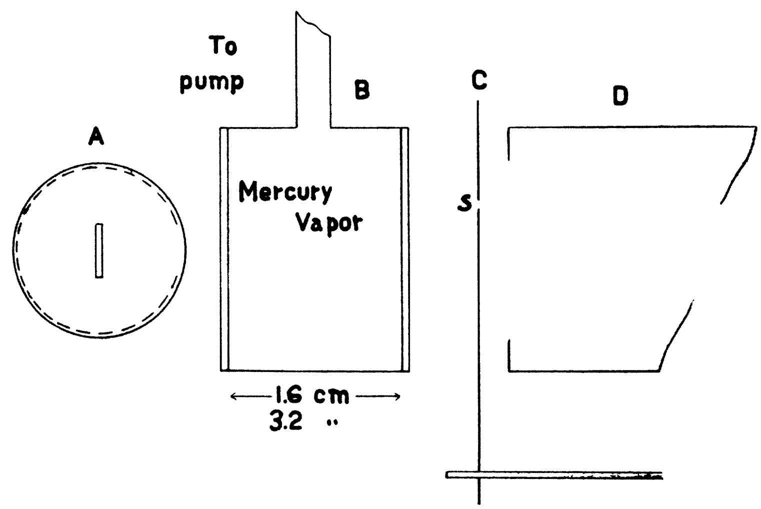

Fig. 1. Arrangement of photographic apparatus.

containing mercury vapor was placed between the source and the quartz spectrograph *D*. A disk *C* having near its circumference a small hole *S* which upon rotation of the disk passed the end of the collimator tube of the spectrograph, acted as a long slit, different parts of which corresponded to different instants of time. This disk was mounted on the axis of a commutator and could be adjusted with respect to the commutator so that the potential exciting the source could be removed at any desired point in the field of view of the spectrograph. The curved trace on the photographic plate beginning at this point revealed the subsequent history of the radiation. The speed of the disk and the law of blackening of the photographic plate were alone needed for quantitative measurement of the rate of decay of the radiation.

Apparatus

The mercury arc source was contained in a commercial quartz flask of 150 cc capacity, having a neck, 1.8 cm inside diameter and 9 cm long, sealed with DeKhotinsky cement to a hollow brass plug which was sealed in turn to a glass tube supporting the electrode wires and pumping tube. The flask was mounted in an upright position with a small amount of mercury in the bottom. An electric heater surrounded the bulb. The temperature of the flask was measured by means of a copper-constantan thermocouple attached to the outside of the bulb. The vacuum system consisted of a diffusion pump and forepumps. All observations were made at gas pressures below the limit of a McLeod gauge connected to the flask.

The source of electrons was an equipotential hot cathode of oxide coated platinum. The heating element was of 0.05 mm platinum, and insulated from it by mica was a sheath of 0.16 mm platinum making electrical contact with the heater at one end by a tongue. The sheath was coated with barium and strontium oxides. Heating currents of from 9.5 to 13 amp. were used. Such a cathode gave ample emission at bright red heat and lasted several months under almost daily use with arc currents as high as 2 amp. The anode was a cylinder of nickel gauze, 1.6 mm spacing, 1.8 cm in diameter and 6 cm long. For testing the behavior of the radiation excited in the cells it was necessary to have the arc in a tube of small diameter in order to insure that the radiation from the arc would decay very rapidly upon removal of the exciting potential. The electrodes were, therefore, suspended in the neck of the flask, the anode being in contact with the quartz wall. The radiation passed to the optical system through a slit in the anode.

Since each record on the photographic plate was composed of hundreds of superimposed photographs, it was essential that the commutator and disk be accurately constructed. An excellent commutator was built by the research mechanician, Mr. S. Cooey. The heavy commutator disk, 12.7 cm in diameter and 2.5 cm wide, was divided into 24 sections separated by 0.8 mm of mica, accurately spaced to about .0025 mm. Each section could be connected to either of two slip rings, thus providing for an exciting and a reverse potential. The contacts to the commutator and slip rings were made by hard carbon brushes. The brush on the commutator was ground to a knife edge and placed perpendicular to the surface so that the bearing edge was not more than 0.5 mm wide. The shaft was mounted in ball bearings and the whole so nicely balanced that it was run for periods of three or four hours without appreciable chattering or heating, even at speeds as high as 70 r.p.s.

The disk C was of aluminum, 20 cm in diameter, and was mounted on a steel face plate at the end of the shaft. Corresponding to each pair of commutator sections was a hole (S, Fig. 1), 0.3 mm in diameter, the small size being necessary to obtain sufficient resolution in time.

Two cylindrical quartz cells (See Fig. 1) with plane polished ends were used for the study of the radiation excited by resonance. In diameter they were 2.5 cm, and in length 1.6 cm and 3.2 cm, respectively. These cells will be referred to as the short and long cells, respectively. Connection to the vacuum system was provided by a stem in the middle of each. For temperature control this stem was jacketed close to the cell.

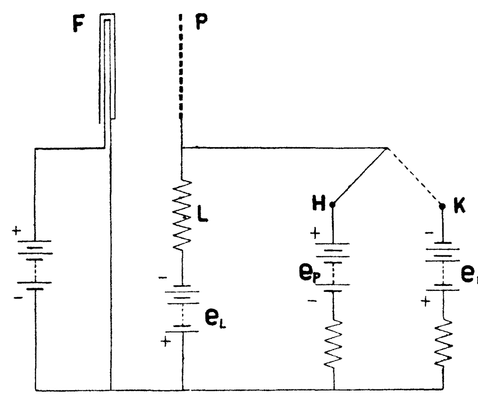

Fig. 2. Electrical circuit of the arc.

Experimental Procedure

The essentials of the electrical circuit of the arc are shown in Fig. 2. P is the anode and F the filament. Two adjacent segments of the commutator are represented by the points H and K. While P was in contact with H, usually about 7×10^{-4} sec., the arc was excited by a positive potential e_p. As the brush passed from the segment H, the positive potential was removed from P, and after an interval of time corresponding to the passage of the brush over the mica section, the reverse potential e_r was applied by the segment K. The commutator and disk were adjusted so that the positive voltage cut-off came after the hole in the disk had traced a line several millimeters long on the photographic plate. The exact position of this cut-off was determined from a photograph made while rotating the disk slowly by hand. To test the uniformity of the different parts of the arc, etc., a check photograph with the disk rotating but with an uninterrupted positive voltage on P, was taken on each plate. This was necessary since patches of unusually intense radiation were occasionally observed in the arc, and there were blemishes in the windows of the quartz cells.

Precautions were taken to eliminate errors due to sparking as the brush left the "live" section of the commutator, and to leakage over the mica insulation. Most of the photographs were taken at arc currents of a few tenths of an ampere, so that with a non-inductive circuit, sparking was reduced until it was barely visible in a darkened room. Again, a leak L, with or without a reverse voltage e_L, was introduced to take care of the period during which the brush was on the mica insulation. Also, reverse voltages were maintained on the "dead" commutator sections. Out of at least 50 photographs of the arc alone, some with exposures of several hours, not one gave evidence of faults in commutation. Furthermore, the entire mica insulation corresponded to only 1 mm on the plate, whereas with the long cell in the system the persistent radiation caused a trace 15 mm in length. The effect of vibration of the commutator system with respect to the photographic plate was found to cause an error on the plate of only 0.2 mm, corresponding to an error of less than 3×10^{-6} sec.

Photographs of the arc with electrodes in the neck of the flask were first taken as described above. The quartz cell was then introduced between the arc and the disk and photographs taken as before, using each cell at various speeds of the disk, with temperatures ranging from 40°C to 100°C.

The photographic densities on the plate were measured by means of a small bismuth-silver thermocouple mounted as the cross-hair in a microscope of approximate magnification 2. This magnification, together with the small size of the thermocouple, 1/3 mm by 1/6 mm, gave sufficient resolution for measurements with even the most rapid rate of decay observed.

The photographic densities were translated into intensities by means of test plates developed either in the same bath or under similar conditions. The exposures on the test plates were obtained by photographing a mercury arc of constant intensity for varying intervals of time. The photographs to be measured, on the other hand, were made under the condition of a constant exposure time but varying intensity. It is well known that for very short times of exposure or for very low intensities the reciprocity law no longer holds, but the work of Harrison and Hesthal[2] shows that for panchromatic films in the wave-length region under consideration the density-log time curves and the density-log intensity curves have the same slope over their linear portions. Only those plates were chosen for measurement, therefore, whose densities lay on the straight part of the density-log exposure curve. When the check photographs, taken with an uninterrupted positive voltage on the anode, showed variation in density over the length of a trace, a correction was applied to reduce to a uniform initial intensity.

Results

The intensity-time relation for $\lambda 2537$ from the arc alone is shown by Curve (*a*), Fig. 3, starting from the instant of commutation. The intensity of the radiation falls off in a manner approximately exponential with the exponential constant 1.7×10^5 sec.$^{-1}$ This gives the time constant 0.6×10^{-5} sec. Besides a strong absorption of $\lambda 2537$, the effect of the introduction of the cells into the path of the radiation was to decrease the rate of decay of that line. The longer cell produced the greater change. Curve (*b*) shows the decay of the radiation for the short cell in the system and Curve (*c*) that for the long cell. These curves show an approximately exponential decay with the time constants 4.0×10^{-5} sec. and 6.8×10^{-5} sec. for the short and long cells respectively. These times are roughly proportional to the lengths of the cells. The above curves are each the average of determinations made from several plates, and are not in error by more than 10 to 15 percent.

The persistent radiation from the arc directly transmitted through the cell after the cutting off of the voltage was insufficient to account for the persistence found with the cells. Curve (*a*) Fig. 3 shows a measurable persistence of $\lambda 2537$ from the arc, but the rate of decay of this radiation was so rapid that at the time when the radiation measured with the long cell in the path had fallen to $1/e$ of its initial value, the arc radiation, even if uncorrected for absorption, would have been present with only 1/7000 the intensity actually observed. If corrected for the cutting down of the radiation from the arc by the mercury cell, about 98 percent as measured by the relative exposures necessary to give equal plate densities with the arc alone and with the cell in the path, the primary radiation is seen to be entirely negligible

[2] Harrison and Hesthal, Jour. Opt. Soc. of Am., **8**, 471, (1924).

after the first 2×10^{-5} sec. As a further check a photograph of the arc was made with the length of exposure necessary to produce a measurable plate with the long cell in the path. The trace on this much overexposed plate had entirely disappeared at a time at which radiation of considerable intensity still persisted with the long cell in the system. These facts show clearly that practically all the persistent radiation coming from the cell was due to some process of absorption and reemission by the vapor in the cell. The shape of the decay curve for

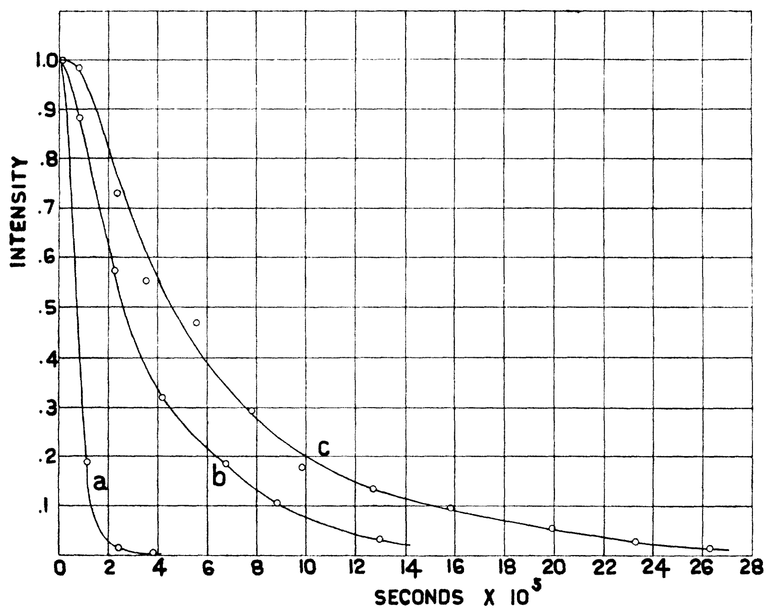

Fig. 3. Rate of decay of λ2537 from the source alone (a) and with the shorter cell (b) and the longer cell (c) in the system.

the first 2×10^{-5} sec. is distorted, however, by the persistent radiation from the arc. No correction can be made, since the method of correction depends upon the unknown processes involved in the persistence.

Over the range of cell temperatures investigated, 40° to 100°C, the rate of decay of λ2537 was found to be independent of the pressure as measured by the temperature at which the mercury condensed in the stem of the cell. The body of the cell was maintained at a higher temperature to prevent condensation on the faces. Thus the temperature of the liquid mercury in contact with the cell wall was always higher than that of the stem, so that the vapor pressure of the mercury in the cell was higher than that corresponding to the temperature of the water jacket on the stem. That variation in the vapor pressure in the cell was brought about by the change in temperature of the water jacket is certain, since between the lowest and the highest temperatures employed there was a twenty-fold decrease in the transmission of λ2537.

It is of interest to note that upon introduction of the cell into the system the increased persistence of λ2537 was observed only when mercury from a drop in the cell was distilling into the stem connected with the vacuum pump. A photograph taken with the cell free from liquid mercury, but connected with the pump so that it contained mercury vapor at about 30°C, showed considerable absorption of λ2537 but no persistence greater than that accounted for by the arc alone. The explanation that at once suggests itself is that the persistence is present only near the surface of distilling mercury. Yao[3] found this condition necessary for the striking of a low voltage arc at 4.9 volts. Doubt is thrown upon this explanation by other photographs taken after the cell had been thoroughly baked, pumped and sealed off. In this case also there was no increased persistence, although mercury was distilling freely into the jacketed stem. It is possible that the condition for the slow decay is not the presence of freshly evaporated mercury vapor, but is the absence of traces of air or water vapor which might have been introduced during the sealing-off process. The cell, containing liquid mercury and connected with the pump, would constitute in itself an effective diffusion pump, so that only extremely pure mercury would be present in the body of the cell. It is well known that a small amount of air is effective in quenching the radiation λ2537 excited by resonance.

Discussion

Lack of data relating to the exceedingly complex processes involved in the persistence of radiation in a vapor makes an exact description of these processes impossible at present. The nature of the process of absorption of radiation by an atom and the effect of molecular impact during or after absorption are not understood. The character and the amount of dissipative absorption are not known. In the experiment described above all the lines of the arc spectrum were present during the period of excitation. Since these lines are absorbed by excited vapor it is probable that they play some part in the persistence.

There is reason to expect the presence in the cells of metastable atoms in the $2p_1$ and $2p_3$ states, resulting either from impacts of normal

[2] Y. T. Yao, Phys. Rev. **21**, 1 (1923).

mercury atoms with excited atoms in the state $2p_2$ or from the absorption of the strong arc line $2p_2-1s$ which lifts the electron to the $1s$ orbit from which two of the three possible transitions leave the atom in the metastable states $2p_1$ and $2p_3$.[4] The effect of impacts with the metastable atoms would be, in part, reversion to the $2p_2$ state and subsequent emission of λ2537. There is also the possibility of a mercury molecule formed by impact of a normal atom with an atom in the $2p_2$ state, although neither the ultra-violet nor green bands characteristic of the fluorescence of mercury at high pressures, and attributed to Hg_2, appeared on the plates or to the eye.

It is not clear, however, how the persistence of λ2537 may be related to the presence of such metastable atoms in the vapor. One possibly significant fact is, however, to be noted with regard to the above results. The times involved in the rate of decay of λ2537 were of the order of magnitude of the times required for atoms, having the mean velocity corresponding to the temperature used, to traverse the cell without impact. At 75°C the mean velocity of mercury atoms is 1.9×10^4cm/sec. In the case of the cell of length 1.6 cm, an atom would, on the average, traverse a distance equal to the length of the cell in 8.4×10^{-5} sec. For this cell the time constant was 4.0×10^{-5} sec. If, instead of the total length of the cell, the mean length (one-half) is taken, this mean time is 4.2×10^{-5} sec., which is very nearly equal to this time constant. In the case of the long cell the agreement is not so close but the times are still of the same order of magnitude. The experimental curves correspond closely with those calculated on the assumption of a uniform initial distribution of excited atoms throughout the cells and of the passage without impact of these atoms to the walls of the cell, where the energy of excitation is freed as radiation. However, with the vapor pressures used the probability of such a passage without impact is so small that such an explanation of the results by diffusion of excited atoms seems impossible, unless some new factor be assumed such as the compensation of the slower passage of the excited atoms, due to impacts, by the dissipation of the persistent radiation at impact.

Since the whole persistent process depends initially upon the absorption of λ2537, one would expect at least a part of the persistent radiation to result from repeated absorption and re-emission. Wood has shown that there is such diffusion of radiation in mercury vapor at .001 mm pressure.[5] If this is the only process effective, however,

[4] R. W. Wood, Proc. Roy. Soc. **A106**, 679 (1924).

[5] R. W. Wood, Phil. Mag. **23**, 689 (1912).

the absence of any dependence of the rate of decay on vapor pressure is difficult to account for, unless we may assume some compensating process such as dissipation at impact or a change in the wave-length of radiation emitted during impact. Even at a pressure as low as 001 mm the probability of a quantum of radiation diffusing through the cell without being associated with an atom at impact is small. There is evidence[6] for the dissipative effect of impacts in the decreased intensity of λ2537 excited by resonance absorption in pure mercury vapor at high pressures. At very high vapor pressures the time between impacts may determine the order of magnitude of the persistence, while between the low and high extremes of pressure there is possibly a pressure range over which only a small variation in rate of decay might be observed.

Persistent Radiation from a Mercury Arc

A study of the rate of decay of λ2537 from an arc struck at the center of a mass of mercury vapor, approximately a sphere 6 cm in diameter, was also made. The same quartz flask was used, but the hot cathode and anode were supported at the center of the bulb and a third electrode, a nickel mesh, lined the spherical quartz wall. By a method similar to that employed with the cells, photographs were taken at temperatures from 70°C to 150°C with several voltages on the outer electrode and several different reverse voltages on the anode after commutation.

The curves in Fig. 4 show the rate of decay of λ2537 from this arc. The persistence was very much longer than that observed with the arc in the neck of the flask. The curves are, like those for the cells, approximate exponentials, the time constant in this case being 5.5×10^{-5} sec. The difference between the geometry of the spherical bulb and that of the cylindrical cells makes any comparison involving dimensions very difficult. It is to be noted that the difference of potential between the electrodes after commutation made not the slightest difference in the rate of decay. The same curves were obtained for an open circuit as for reverse potentials from 1 volt to 50 volts. There seems, therefore, little doubt that the persistent radiation λ2537 in the mercury arc was due to the same cause as that in the cells, and is not to be explained by space charge conditions or recombination.

[6] Wood and Kimura, Phil. Mag. **32**, 329 (1916).

It is also to be noted that within the limits of experimental error the rate of decay of λ2537 from the arc in the bulb of the flask was independent of the vapor pressure over a range of pressures from .05 mm to 1.7 mm. The curve in Fig. 4 is drawn through points taken from photographs at 78°C, 100°C, and 140°C, as measured by a thermocouple attached to the outside of the bulb near the liquid mercury. Since the seal at the top of the neck of the flask was water cooled, there was considerable condensation at that point, so that the pressure of the mercury vapor was less than that corresponding to the temperature measured. The condensation, however, took place several inches from

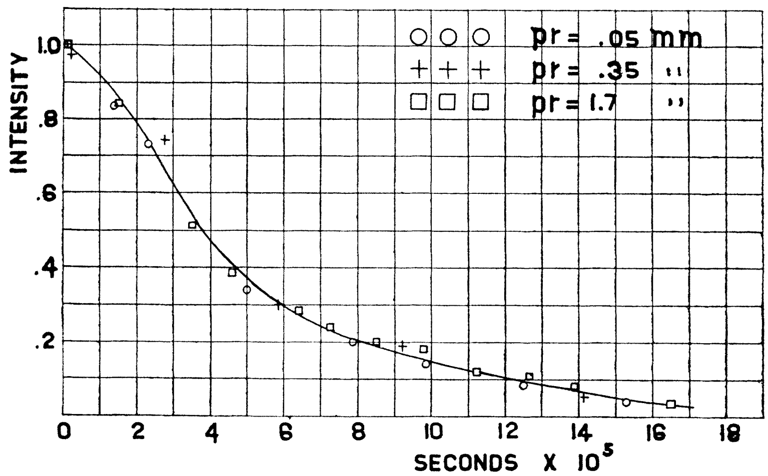

Fig. 4. Rate of decay of λ2537 from the arc in the bulb of the flask.

the top of the bulb, while the electrodes were immediately above the mercury surface. Furthermore, the increase in the intensity of the radiation and the change in the appearance of the arc make it certain that there was a large change in the vapor pressure. The rate of decay was so nearly independent of the vapor pressure that one curve was drawn through the circles, crosses and squares which give the experimental results for vapor pressures, computed as above, of .05 mm, .35 mm, and 1.7 mm, respectively.

At higher temperatures and greater currents the arc emitted after commutation a peculiar many-lined persistent spectrum, which was studied in detail together with the current conditions in the tube after commutation. The results of this study will be discussed in a later paper.

In conclusion I wish to express my indebtedness to Professor H. W. Webb, at whose suggestion and under whose guidance this work was done.

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COLUMBIA UNIVERSITY,
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