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E. E. Stepp and R. A. Anderson, "Decay of Intensity of Certain Hg Lines in an Hg-Ar Discharge," *Journal of the Optical Society of America*, vol. 53, no. 10, pp. 1139-1146, Optical Society of America (OSA), Oct 1963.

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Reprinted from JOURNAL OF THE OPTICAL SOCIETY OF AMERICA, Vol. 53, No. 10, 1139–1146, October, 1963
Printed in U. S. A.

Decay of Intensity of Certain Hg Lines in an Hg–Ar Discharge*

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(Received 10 December 1962)

The afterglow of four mercury spectral lines was examined in a mercury–argon electric discharge. The 2537-Å line decays in a complex fashion with three definite modes of decay. The 4077-, 4358-, and 5461-Å lines exhibited an even more complicated decay. These lines exhibited an initial rapid decay followed by an increase in intensity. Finally the intensity of these lines went through two maxima before they decayed in intensity at a slow constant rate. The actual intensity behavior of the 2537-Å line was masked by the imprisonment of resonance radiation. It is postulated that the main processes governing the initial decay were spontaneous radiative decay coupled with electron and ion repopulation of the excited mercury states. The negative decay constant occurring around 100 μsec was probably controlled by the group action of the following processes: ionization of mercury by argon and the resultant recombination, thermalization of discharge electrons and their resultant recombination, and production of electrons by the interaction of mercury metastable atoms and their recombination. The final slow rate of decay was probably controlled by mercury molecular dissociative recombination.

INTRODUCTION

In recent data[1–3] extensive studies have been made on the afterglow of mercury band systems. The intensity behavior of mercury spectral lines has not been investigated in detail. Much of the data on the afterglow of mercury have not been extended to short times. Interesting features of the decay occur around the time of 100 μsec; a region of time which has not been examined in detail. It must be mentioned that recent investigators have used pure gas samples and microwave techniques.[4] From the data presented in this paper there are indications that spectral lines should be examined in microwave studies at short time intervals, and the electron densities should be measured in the microsecond region. The data presented in this paper has been complicated by the addition of argon gas.

EXPERIMENT

The electric discharge lamp examined was a commercial General Electric 4-W germicidal lamp of the standard U shape. The lamp was operated on direct current. The spectral lines were isolated by using a Bausch & Lomb 500-mm quartz grating monochromator. Figure 1 shows a block diagram of the apparatus.

The lamp was shut off by shorting it with a mercury wetted relay operated at 60 cps. The intensity of the light, at a known time after the lamp was shut off, was sampled by applying a 1200-V 40-nsec pulse to the dynode chain of the 1P28 photomultiplier detector tube. The total charge passed by the photomultiplier tube in one minute (3600 pulses) was stored in a capacitor and the voltage across the capacitor was read out on a Keithley electrometer. The delay time between the lamp shutoff and the application of the pulse to the photomultiplier tube could be set at an value between 2.18 and 3450 μsec.

A pulse technique was used so that the average of a large number of trials (3600) could be used to minimize the effects of shot noise. The experimental procedure is similar to that used by Phelps and McCoubrey.[5]

The external temperature of the discharge lamp was controlled by an external copper heat jacket. Thermal contact between the copper heat jacket and the lamp was maintained by fine copper filings filling the empty space. A small window in the heat jacket at the central position of the lamp allowed light to emerge. The temperature of the walls of the lamp was measured by three thermocouples placed at the top, middle, and bottom of the lamp. The fluid used to heat and cool the lamp was water flowing through the copper heat jacket. By filling all empty space between the heat jacket and lamp with copper fillings, the temperature could be maintained constant over the length of the lamp.

RESULTS AND DISCUSSION

The most interesting region of the decay of the 5461-, 4358-, 4077-, and 2537-Å lines is the region

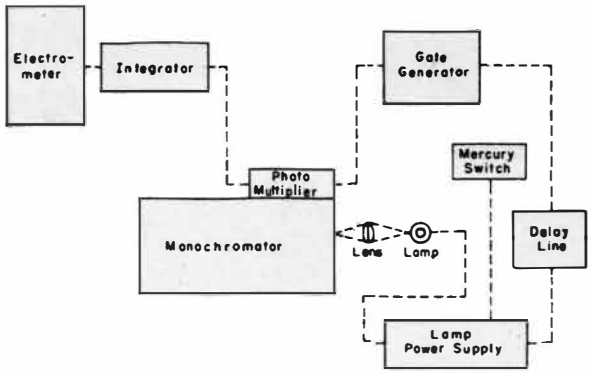

FIG. 1. Block diagram of decay-time apparatus.

* This research was supported in part by the National Science Foundation.

[1] P. Dandurand and R. Holt, Phys. Rev. **82**, 278 (1951).
[2] P. Dandurand and R. Holt, Phys. Rev. **82**, 868 (1951).
[3] M. Biondi, Phys. Rev. **90**, 730 (1953).
[4] M. Biondi and S. Brown, Phys. Rev. **75**, 1700 (1949).
[5] A. Phelps and A. McCoubrey, Phys. Rev. **118**, 1561 (1960).

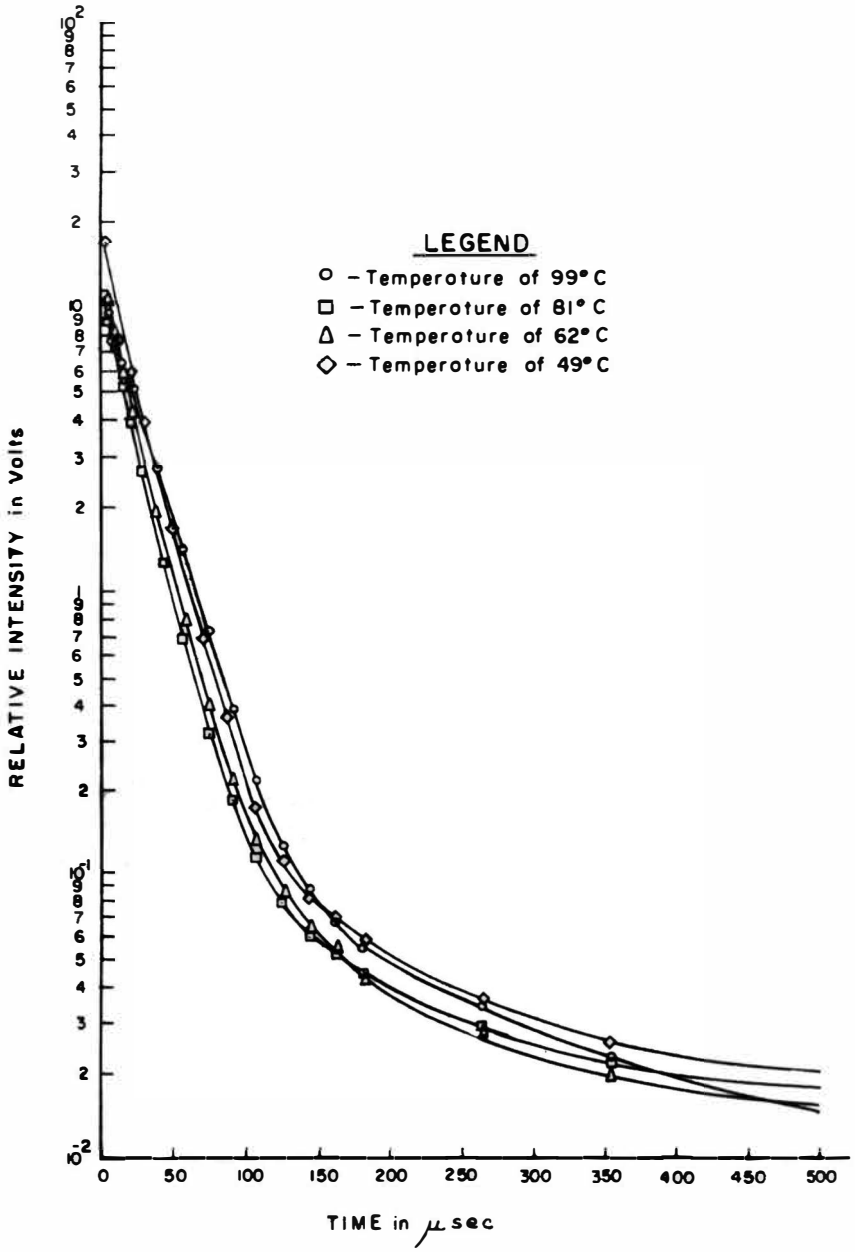

FIG. 2. Decay of intensity of the 2537-Å Hg line versus time.

around 100 μsec and this data can be seen in Figs. 2-6.

In taking this data the slit settings of the monochromator were not the same for all of the lines, but this only led to an over-all change in light intensity and did not effect the shape of the decay curves. Since only the general nature of the decay is discussed and the decay times compared, this is not a major discrepancy. The decay of the 2537-, 4077-, 4358-, and 5461-Å lines was examined at temperatures of 99°, 81°, 62°, 49°, 40°, 30°, 20°, and 8°C; and 100°, 60°, 39°, and 12°C; 99°, 60°, 39°, and 12°C; and 100°, 60°, 40°, and 12°C, respectively.

The decay of all four mercury lines exhibited three modes of decay. The first mode of decay is the initial rapid decay of short time interval. This decay mode is followed by a complicated intermediate mode. The final mode of decay is the slow rate of intensity decrease beyond 300 μsec. The region of greatest interest in the decay for all four lines is the region between 2.18 and 300 μsec. Figures 2–6 exhibit the data taken in this region. The data for the decay around 100 μsec for the 2537-Å line does not agree with the results of Dandurand and Holt.[2] This discrepancy might be caused by the experimental techniques, for they used microwave techniques and pure mercury samples.

The initial rapid decay of all four mercury lines is examined first. The initial decay for times less than 50 μsec was exponential and the light intensity drops by 1/100 of its original intensity in this region. The

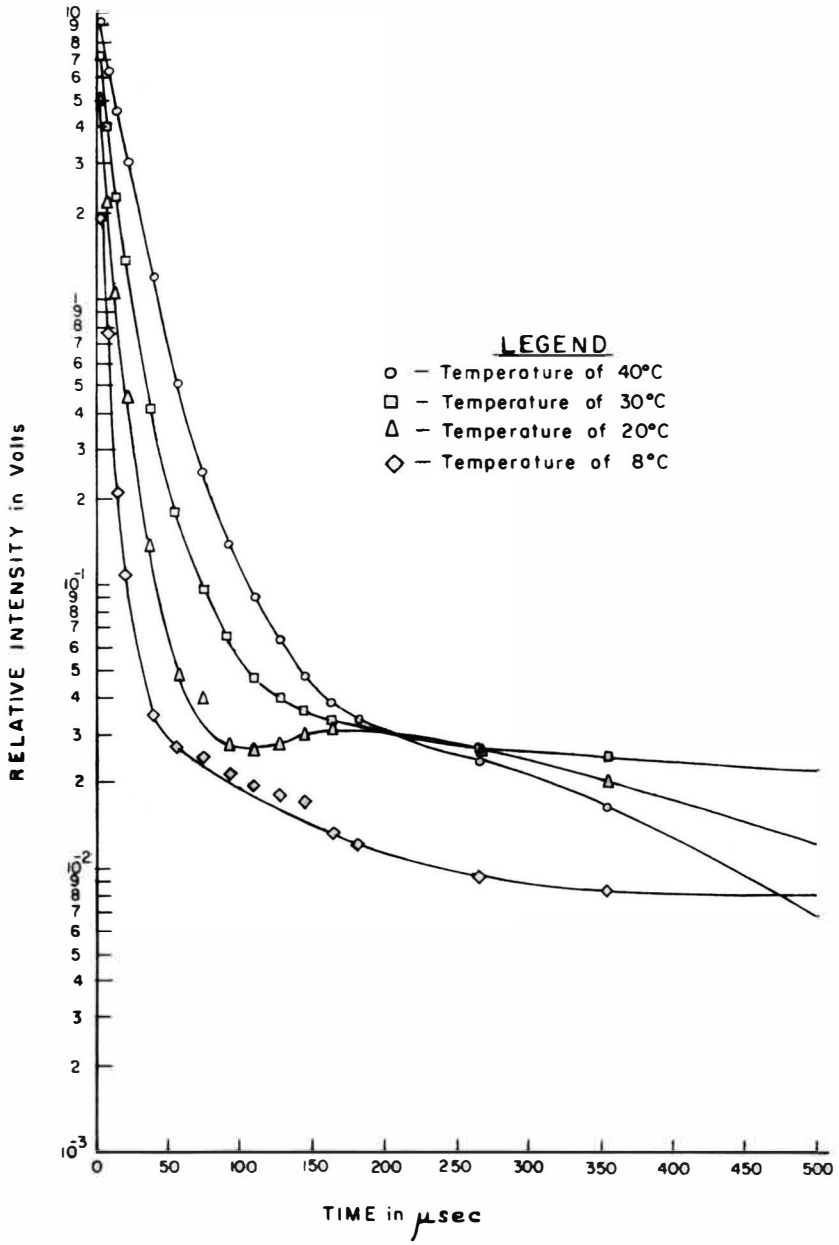

FIG. 3. Decay of intensity of the 2537-Å Hg line versus time.

initial decay of the lines was interpreted from the slope of this initial linear portion on a semilogarithmic plot. The intermediate decay mode had negligible effect on the initial decay. The decay times obtained from the slopes of the initial decay for the four lines are given in Table I.

The initial decay times of these lines are noted to decrease with decreasing temperature which is an expected result. This result is consistent with the decreased mercury density. An increased mercury density would increase the population of these levels through electron excitation of the levels and ionization of the mercury atoms. During the initial time after shutoff of the discharge the electrons have energies sufficient to excite and ionize the mercury atoms. At later times

TABLE I. Initial decay times of the 2537-, 4077-, 4358-, and 5461 Å lines.

Wavelength (Å) / Temperature (°C)	2537	4077	4358	5461
		Decay time (μsec)		
100		12.5		13.6
99	32.9		11.8	
81	30.3			
62	21.9			
60		9.82	8.93	10.5
49	19.1			
40	16.8			7.28
39		6.36	6.24	
30	11.5			
20	7.88			
12		2.79	1.92	1.78
8	5.19			

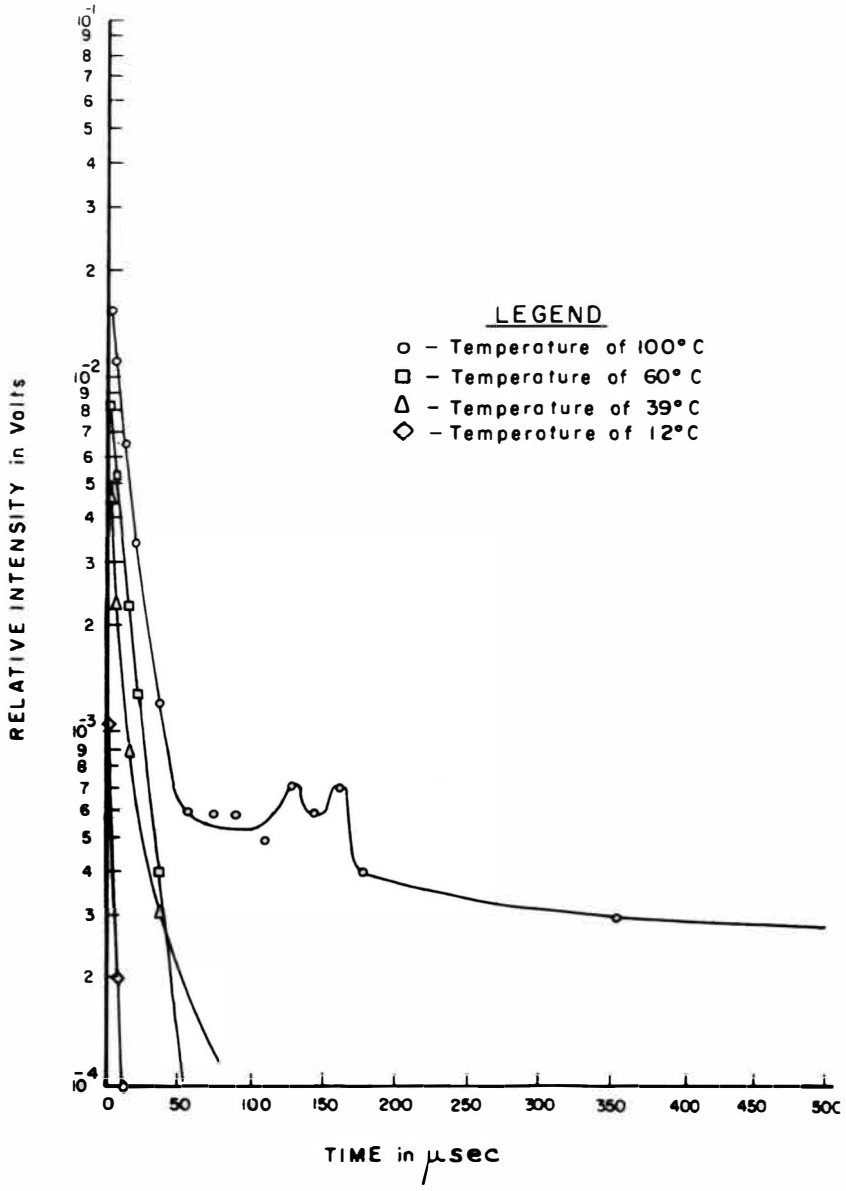

FIG. 4. Decay of intensity of the 4077-A Hg line versus time.

the electrons would become thermalized. Also the excited argon atoms would ionize the mercury atoms. All of these effects depend on the mercury density in the lamp.

In the case of the 4077-, 4358-, and 5461-Å lines, the decay times are not of the same order of magnitude as the spontaneous emission decay times. They are 10 to 100 times greater. This persistence of these lines is consistent with the excitation processes of the mercury atoms given in the last paragraph.

If the decay times are compared between the 2537-Å line and the 4077-, 4358-, and 5461-Å lines, the decay times of the 2537-Å line are longer. The nonresonant 4077-, 4358-, and 5461-Å lines have nearly the same decay times at corresponding temperatures. The 2537-Å line is a resonant line of mercury and this line is imprisoned in the lamp. The decay time because of this imprisonment increased with increased mercury density and temperature. This imprisonment of the resonant line caused the decay times to be longer for this line and caused the enhanced temperature dependence of the decay times for this line. In a discharge the decay of this resonant line is not totally controlled by spontaneous emission and the imprisonment of resonance radiation, and the decay time will not be directly proportional to the atomic density and the radius of the discharge tube.[5,6] Since the 6^1P_1 level from which the 2537-Å line originates is populated by transitions corresponding to 4077- and 5461-Å lines, the 2537-Å

[6] T. Holstein, Phys. Rev. 72, 1212 (1947); 83, 1159 (1951).

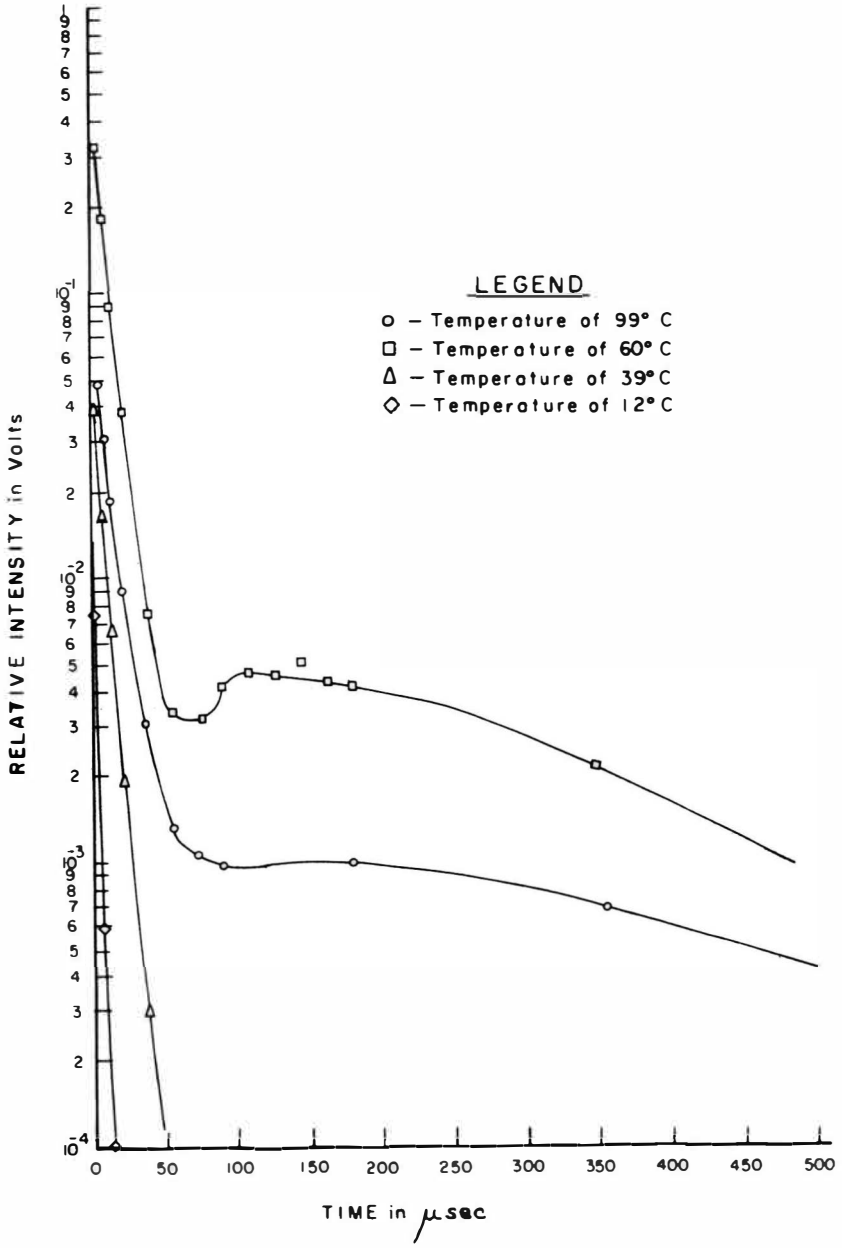

FIG. 5. Decay of intensity of the 4358-Å Hg line versus time.

lines would have a decay time similar to these lines if imprisonment did not occur.

In Fig. 7 the decay times of the four lines were plotted versus mercury density. Since the decay times of the 4077-, 4358-, and 5461-Å lines are similar, the curves exhibit similar behavior. The 2537-Å curve resembles the curves of the other three lines, but a more abrupt change in slope occurs at the deflection point. This is probably caused by the imprisonment of the 2537-Å line.

It should be mentioned that the higher-order 4077-, 4358-, and 5461-Å lines have a smaller intensity than the resonant 2537-Å line. This result is expected since the emission of radiation from the 6^3P_1 level is the main manner in which the atoms decay to the ground state. Only two of the higher-order lines examined decay into the 6^3P_1 level; there are many other transitions from higher levels populating this state.

The intermediate region of decay of interest is around 100 μsec. From previous results[2] it was expected that the mercury intensity would exhibit two decays, a short lifetime decay and a long lifetime decay. In the region around 100 μsec all lines show the effect of some process which is populating the levels from which the lines originate.

In this region the intensity behavior of the 2537-Å

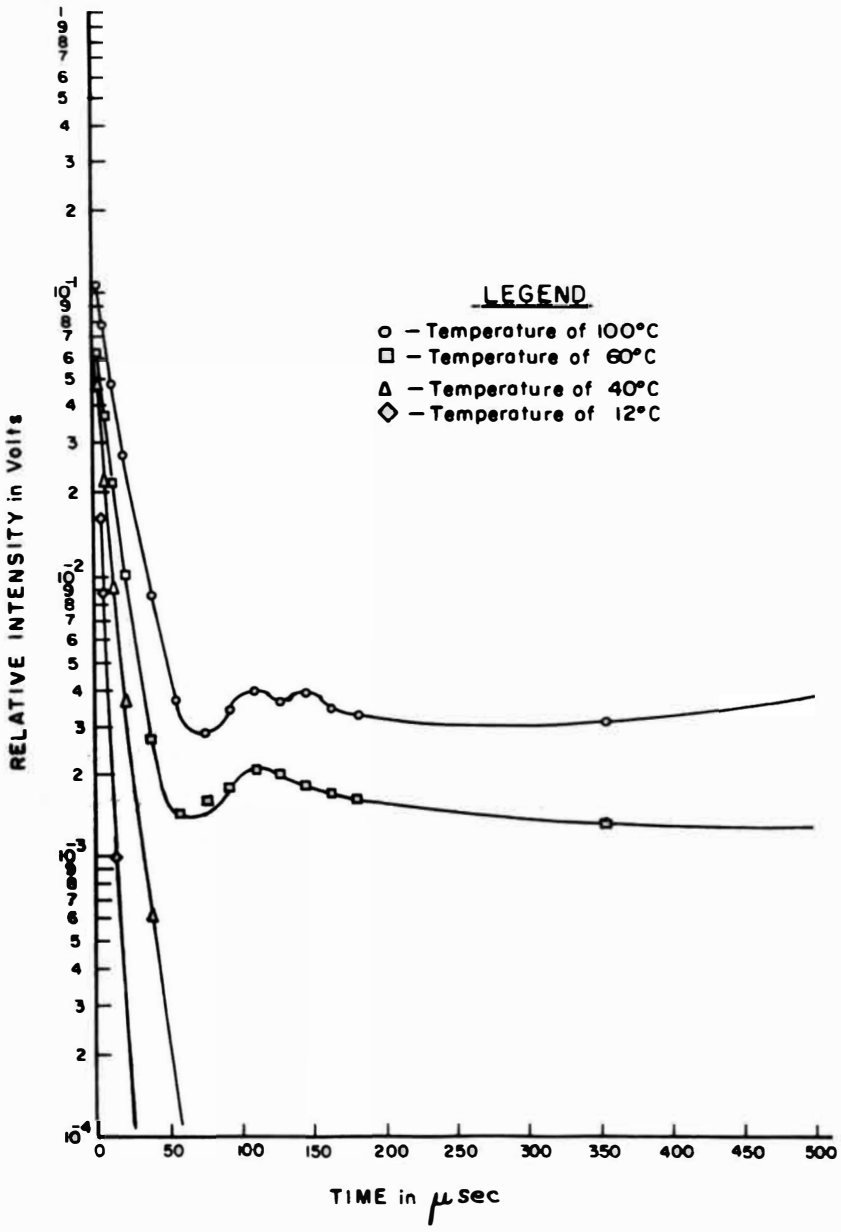

FIG. 6. Decay of intensity of the 5461-Å Hg line versus time.

line is discussed before the other lines are considered. In most cases the intensity became nearly constant, and at the two low temperatures the intensity actually increased. The 20°C decay curve has been analyzed in detail. The decay curve of the line at this temperature can be represented by an equation of the form

$$I = A\exp(-\alpha t)+\exp(-\beta t)\left[\frac{1-\exp(-\gamma t)}{at+b}\right]. \quad (1)$$

This equation can also be used to represent the data at 8°C, but it does not completely represent the curves above 20°C. The break down of this equation for higher-temperature curves is probably caused by the increased imprisonment of this line at high temperature. The imprisonment of the resonant line is more dominant than the populating processes in this region. The first term of Eq. (1) corresponds to the initial rapid decay of intensity. The second term can be interpreted as the radiative decay of atoms which are recombining with an increasing source of electrons. The source of electrons for recombination in this region of the decay has been examined by Kunkel.[7] The possible reactions which can produce electrons are collisions between unexcited mercury atoms and excited meta-

[7] W. Kunkel, Phys. Rev. 84, 218 (1951).

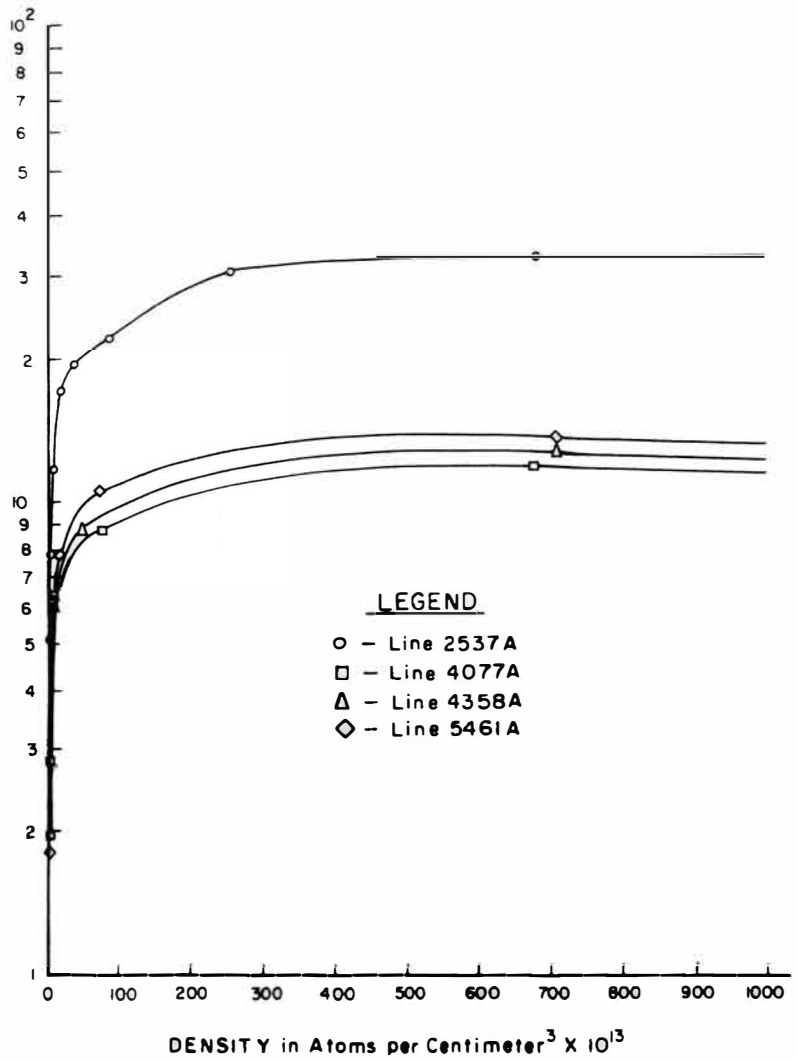

FIG. 7. Decay times of the four Hg lines versus Hg atom concentration.

stable argon atoms and the collision of two metastable 6^3P_2 mercury atoms.

$$Hg+Ar_m \rightarrow Hg^+ + e^- + Ar, \quad (2)$$

$$Hg_m + Hg_m \rightarrow Hg^+ + e^- + Hg. \quad (3)$$

Two sources of electrons for recombination are indicated and this is further discussed for the decay of the other lines.

In the decay-time region around 100 μsec for the 4077-, 4358-, and 5461-Å lines the intensity of the light increases, reaches a maximum, decreases to a minimum, and then increases in intensity to a second maximum before it finally decays at a slow gradual rate. The double maximum in the decay curve would indicate that there are probably two processes which produce increased electron population in this time region. The increased electron population would produce increased recombination and line intensity. The 2537-Å line exhibited only one maximum, but imprisonment of radiation could mask the dual maxima. As indicated in the discussion of the 2537-Å line these maxima might be produced by the reactions given in (2) and (3).

$$Hg+Ar_m \rightarrow Hg^+ + e^- + Ar,$$

$$Hg_m + Hg_m \rightarrow Hg^+ + e^- + Hg.$$

From Figs. 4–6 it is apparent that the electron production processes are temperature dependent. Further, since these maxima appear only at high mercury temperatures, this indicates that they are dependent on mercury atom concentration. Also it is only at the high mercury temperatures that there is appreciable metastable atom concentrations, so that the reaction of Eq. (3) can occur.

It should be mentioned that reactions of the type indicated by Eqs. (2) and (3) are probably responsible for the intensity behavior in the intermediate region. Equation (1) has only one electron production term

TABLE II. Long-interval decay times of the 2537-, 4077-, 4358-, and 5461-Å lines.

Wavelenght (Å)	2537	4077	4358	5461
Temperature (°C)		Decay times (μ sec)		
100		500		
99	501		417	419
81	562			
62	643			
60			511	488
49	752			
40	703			
30	663			
20	603			
8	774			

included and to apply this equation to the 4077-, 4358-, and 5461-Å lines would require the addition of a second electron production term.

The final region of decay for all four lines is a long-lived decay. This region of decay is probably controlled by molecular dissociative recombination. The intensity of the lines decrease with decreasing temperature for long decay times indicating the decreased molecular concentration. Some representative decay times at various mercury temperature are given in Table II. At all temperatures the long decay times are of the same order of magnitude. From the table it appears that shorter decay times are generally observed for the higher mercury temperatures and mercury concentrations. At high mercury concentrations there would be increased mercury ion and molecule concentrations and increased recombination. This would shorten the decay times for higher mercury temperatures.

SUMMARY

If the imprisonment of resonance radiation is neglected, the intensity of the mercury lines in a mercury–argon discharge exhibits a complicated decay. The initial decay of the lines is governed by spontaneous emission, and the lines are sustained by argon ionization of the mercury and by electron excitation and ionization. In the region around 100 μsec there are two processes which increase electron concentrations. This fact is verified by the two intensity maxima observed for the 4077-, 4358-, and 5461-Å curves. In additional studies electron concentrations, argon ion concentration, and metastable mercury atom concentrations must be measured. The final decay time of the curves is probably due to molecular dissociative recombination, but this will have to be verified by additional experiments.