eters F_2 and F_4 which are to be so selected as to fit the observed data as well as possible. The values of F_2 and F_4 used for the calculations in the first column were so chosen as to fit ^3H and ^3G of V I exactly. The fifth column is based on a corresponding choice for Cr II instead of V I. In the case of vanadium, $^3F_-$ and $^3P_-$ proved to be in the wrong order as compared with the observed values. However, this situation can be rectified by changing slightly the values of F_2 and F_4, as is evident from the second column of the table. The agreement for ^3H and ^3G is, of course, then to a certain extent impaired. The calculated positions of the terms not yet found experimentally should not be taken too literally, as the parameters cannot be fixed with any precision from the existing experimental data. Nevertheless it has seemed advisable to tabulate these computed positions since they at least show the general trend of the various states belonging to the configuration. Part of the inability to fit the few observed levels very accurately may be due to perturbations by other configurations. In particular, the actual value of ^3G for V II may be abnormally high because of perturbation by the known $3d^34s$ ^3G level at 14,573 cm^{-1}. It is hard, however, to see how the displacement due to this perturbation could amount to more than 800 cm^{-1}. In the case of Cr II, the position of $^3F_-$ may be abnormally low, as the ^4F term from which it is obtained is, no doubt, strongly perturbed by the d^5 ^4F level located about 1600 cm^{-1} above the former. There is no reason why the parameters F_2 and F_4 should have exactly the same values in V I and V II, or in Cr II and Cr III, as the addition of the $4s$ electron may influence the core d^4 to a slight extent. The experimental values for Cr II and Cr III are remarkably nearly equal.

The writer wishes to express his sincerest thanks to Dr. J. H. Van Vleck for suggesting this problem.

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Effect of Temperature and Pressure on the Mercury Afterglow

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Measurements have been made on the rate of escape of resonance radiation from a slab of mercury vapor 4.0 cm thick. The measurements extended over a range of pressures from 0.133 to 0.720 mm of mercury and over a range of temperature from 390°K to 585°K. Calculations have also been made of the decay constants on the basis of Kenty's theory of radiation diffusion. The variations of the disagreement between the experimental results and Kenty's theory as affected by both pressure and temperature are hence made available. Some of the difficulties for present theories in the interpretation of the experimental results are pointed out.

INTRODUCTION

DURING the last few years several studies[1] have been made on the rate of escape of resonance radiation from a slab of mercury vapor after the initial excitation has been cut off. These experiments are in agreement in showing, that for low vapor pressures, the decay constant, β, of the exponential curve representing the decay of resonance radiation emitted by the mercury vapor, decreases as the mercury vapor pressure increases. As the mercury vapor pressure is further increased, the decay constant passes through a minimum value after which it slowly rises with increased vapor pressure.

The final interpretation of these results has not as yet been definitely fixed. In his earlier work Zemansky[2] interpreted his results on the basis of repeated atomic absorptions and re-emissions; the increase in β at higher pressures

* Part of a dissertation presented for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

[1] H. W. Webb, Phys. Rev. **24**, 113 (1924); L. J. Hayner, Phys. Rev. **26**, 364 (1925); H. W. Webb and H. A. Messenger, Phys. Rev. **33**, 319 (1929); H. W. Webb and H. A. Messenger, Phys. Rev. **40**, 466 (1932); E. W. Samson, Phys. Rev. **40**, 940 (1932).

[2] M. W. Zemansky, Phys. Rev. **29**, 513 (1927).

was thought to be connected with the quenching of excited states. Later Zemansky[3] re-interpreted his results on the basis of a metastable atom theory in which the radiation emitted from the cell after cut-off was regarded as being due to the raising of metastable 6^3P_0 atoms up to 6^3P_1 state. On this theory the decreasing values of β in regions of low vapor pressure was believed to be due to the reduction in the rate of diffusion of metastable atoms to the walls of the experimental tube; the increase at higher vapor pressures was thought to be due to the destruction of metastable atoms by being raised from the 6^3P_0 to the 6^3P_1 state.

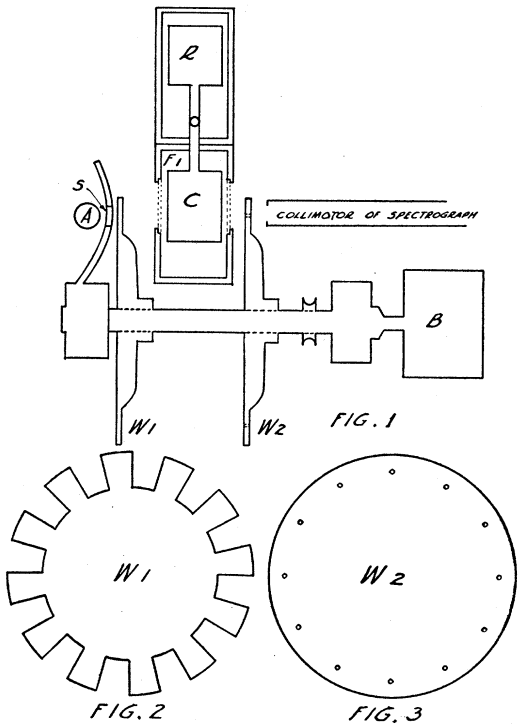
Recently Kenty[4] has given an additional theory of such experiments in which he devises a means of calculating the equivalent opacity of a slab of mercury vapor to resonance radiation as affected by the Doppler broadening of the emission and absorption line, assuming the motions of both absorbing and emitting atoms to have a Maxwellian distribution. Such values of the equivalent absorption coefficient when used with Milne's theory of radiation diffusion lead to predicted values of the exponential decay constants. Zemansky[5] has calculated the decay constants to be expected in his experiment on the basis of Kenty's theory and finds agreement as to order of magnitude between theory and experiment particularly in the region of the lower opacities. Marked deviations were, however, noted at the higher vapor pressures and the suggestion was made that Holtsmark or other broadening might be responsible for such discrepancies between theory and experiment.

In view of the unsatisfactory state of the interpretation of such experiments it seems that there is need for further measurements extending over a wider range of pressures and temperatures than has heretofore appeared in the literature. It is the purpose of the present paper to report additional measurements of this kind. In view of the success of Kenty's theory for the lower opacities, already referred to, it seemed desirable to extend the comparison to the results herein reported. It is hoped that this procedure will give some indication as to the modification required in the present theories of the diffusion of resonance radiation through mercury vapor.

[3] M. W. Zemansky, Phys. Rev. **34**, 213 (1929).
[4] C. Kenty, Phys. Rev. **42**, 823 (1932).
[5] M. W. Zemansky, Phys. Rev. **42**, 843 (1932).

Experimental Arrangements and Procedure

The apparatus shown in Fig. 1 is essentially the same as that used by Zemansky.[2] A is a vertical type water-cooled and magnetically deflected Uviarc mercury lamp. The total radiation from this lamp passed through a horizontal slit S, and a quartz window of a furnace F_1 into a cylindrical resonance cell C. The cell (Fig. 4) was of clear fused quartz with circular plane face 5 cm in diameter, 4.0 cm deep and was mounted as shown in the furnace F_1. F_2 and F_3 were furnaces to control the temperature of other parts of the tube as shown. H is a quartz to Pyrex seal and M is a small iron ball that could be pulled up into the ground glass socket by means of an electromagnet. In this way the tube could be sealed off during a run and the vapor pressure of the mercury controlled. Furnace F_3 was always 20°C to 30°C above the temperature of F_2. The temperatures of F_1 and F_2 were controlled by the use of two mercury regulators



FIGS. 1, 2 AND 3. Experimental arrangements.

K_1 and K_2, which operated two relays. The temperatures of the furnaces were measured with copper-advance thermocouples. In furnace F_1 thermocouples were placed near the top and bottom of cell C. With the disk at rest no difference was noted in the reading of the temperatures at the various points. On rotation of the disks a difference in temperature was noticed between the sides of cell C. Such temperature differences between the sides were reduced by controlling additional heating elements placed on the sides of furnace F_1. In F_2 a thermocouple was placed at the point of condensation of the mercury in cell R.

The temperature of cell C did not vary during an exposure by more than ± 2°C and that of cell R was held constant to within ± 0.3°C. It required from $1\frac{1}{2}$ to 2 hours for the temperatures to become constant.

Between slit S and the furnace F_1 was a rotating disk 25 cm in diameter with 12 teeth (Fig. 2). This disk alternately transmitted the light and cut it off 12 times per revolution. Mounted on the same shaft as W_1 was a second disk of the same diameter (Fig. 3). This disk contained 12 holes 0.6 mm in diameter placed $\frac{3}{4}$ cm from the edge of the disk. The holes acted as a moving slit for the spectrograph.

B(Fig. 1) was a Model 44 Type A Weston magneto connected to the axle of the disk by gears and connected to a Weston Model 45 meter which had been calibrated by the manufacturer to read in revolutions per minute. The speed of the disk could be read to ± 10 r.p.m.

In order to measure the time after cut-off corresponding to any point on the photographic trace it is necessary to know the relationship between distances along the trace and such elapsed time. To obtain this relationship a small mirror was mounted at the center on the end of the axle of the disks. The mirror was mounted in such a way as to reflect a beam of light onto a galvanometer scale. A series of photographs were made of one of the illuminated holes for different positions along the slit of the spectrograph. The angle through which the disks had been rotated was calculated from the displacement of the reflected beam of light and the geometry of the apparatus. A template was made so that the photographic plate would be moved in such a way that the beam of light of the Moll microphotometer passed through the centers of each of the images at λ2537 of the above exposures. The photograph containing the exposures was run through the microphotometer and the distances between these exposures measured on the microphotometer photographic trace. A curve was plotted between distances on the microphotometer trace and angle of rotation of the disk. By the use of this curve the time after cut-off could be measured directly from the microphotometer trace of an exposure.

To show the relationship between light intensity and the blackening of the photographic plate, the characteristic curve of each photographic plate was plotted. This curve was determined experimentally by exposing the plate to the radiation from another mercury arc after it had passed through a Zeiss step filter calibrated for λ2537 by means of a photoelectric cell and a suitable amplifying system. In order to eliminate any possible error due to the intermittency effect, the density marks were photographed under the same condition as that of the afterglow. A third disk, on separate mounting, of the same diameter as W_2 and containing 12 slits each of 0.6 mm width was rotated in front of a narrow slit placed in the beam of light from a 220 volt Uviarc lamp. Cellophane was placed in the beam of light from this arc lamp so that the intensity falling on the photographic plate would be about the same as that of the afterglow. This disk was always rotated at the same speed as the disk W_2 and the exposure time was the same as that of the experiment, so that the intermittency effect in each case would be the same. Means were provided by which the spectrograph could be returned to the same position in front of the resonance cell for each photograph of the afterglow.

The tubes were baked out for several days at a temperature considerable higher than that to be used in the experiment. The pumps were always in operation while the furnaces were being heated up. After the desired temperature was reached the tube was sealed off from the vacuum system by raising the ball M (Fig. 4) into the socket L by means of the electromagnet.

The exposure time was one hour. During this time the temperatures were read every five

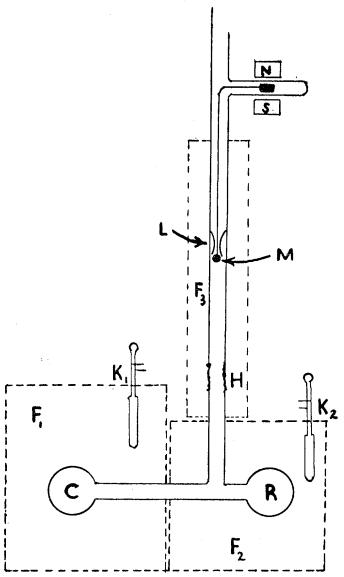


FIG. 4. Quartz cell and furnaces.

minutes and the speed of the disks held constant at 2800 r.p.m. Eastman 50 plates were used.

After the completion of the exposure the spectrograph was shifted in position to make an exposure with the step filter fastened in front of the slit of the spectrograph. This comparison exposure was also of one hour duration and the speed was 2800 r.p.m.

A reproduction of a typical spectrogram is shown in Fig. 5.

Fig. 6 and Fig. 7 are microphotometer traces of the afterglow and calibrating density marks, respectively.

The relative intensities of the radiation emitted by the mercury vapor at different times after the cut-off was obtained by measuring the photographic density at points 0.5 cm apart along each trace: each point representing a known interval of time after the cut-off. This time after cut-off was read from the curve plotted, as previously described, between distance along the microphotometer trace and the angle of rotation, since the angle of rotation is directly proportional to the time.

RESULTS AND CONCLUSIONS

Photographs were taken of the afterglow for various pressures and temperatures as shown in columns 1 and 2 of Table I. A microphotometer

FIG. 5. Photograph of density marks and afterglow.

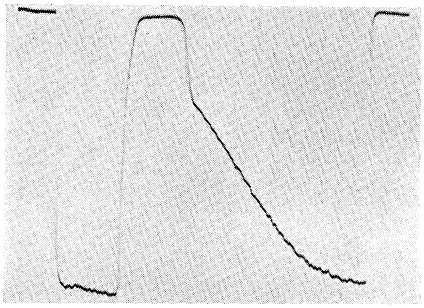


FIG. 6. Microphotometer trace of afterglow.

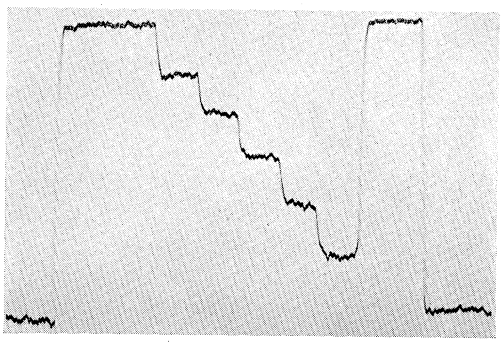


FIG. 7. Microphotometer trace of density marks.

trace was made of each photographic plate as previously described, and the intensity of the afterglow was measured at known intervals of time after cut-off. The curves plotted between the logarithm of the intensities and the time after cut-off gave a straight line. The fact that the first few points after cut-off fall in general below the curve may be due to the fact that certain terms, which enter into the law of decay, persist only for a short time after cut-off. The values of β, either for successive exposures or for exposures with several days intervening, checked within the limits of experimental error

TABLE I. *Experimental and calculated values of decay constant.*

1	2	3	4	5	6	7	8	9
Press. (mm) Hg.*	T (°K)	$N\times10^{-15}$	$\frac{NL}{\Delta\nu_D}\times10^{-7}$	K_0L	$\bar{K}L$	β Theor.	β Exp.	Diff. (Exp. and Theor.)
.133	393	4.34	1.47	1955	112.5	1840	3820	1980
.133	413	4.13	1.36	1809	108.0	1990	4160	2170
.133	435	3.92	1.26	1676	103.0	2200	4460	2260
.133	483	3.53	1.08	1436	94.5	2580	5220	2640
.133	543	3.14	.90	1197	85.0	3240	6390	3150
.133	586	2.91	.81	1077	80.0	3660	7070	3410
.151	393	4.94	1.70	2260	121.5	1570	3170	1600
.151	434	4.48	1.44	1915	111.0	1890	3460	1570
.151	490	3.97	1.20	1596	100.0	2330	3880	1550
.151	529	3.67	1.07	1423	94.0	2640	4220	1580
.151	578	3.36	.94	1250	87.5	3050	5100	2050
.165	393	5.43	1.83	2434	126.5	1450	2900	1450
.165	438	4.87	1.56	2074	116.0	1730	2990	1260
.165	484	4.41	1.34	1782	106.5	2050	3170	1120
.165	531	4.02	1.17	1556	98.5	2410	3280	870
.165	582	3.67	1.02	1357	91.5	2790	3730	940
.238	388	8.09	2.75	3658	158.0	927	2380	1453
.238	435	7.21	2.32	3086	144.0	1120	2400	1280
.238	484	6.48	1.97	2620	132.0	1330	2460	1130
.238	538	5.83	1.68	2234	121.0	1590	2460	870
.238	583	5.39	1.50	1995	116.5	1710	2690	980
.279	398	9.31	3.13	4163	168.0	820	2290	1470
.279	454	8.16	2.57	3418	152.5	990	2290	1300
.279	504	7.35	2.19	2913	139.5	1190	2270	1080
.279	538	6.89	1.99	2646	132.5	1320	2230	910
.279	585	6.34	1.76	2341	128.0	1420	2400	980
.312	396	10.5	3.54	4708	180.0	714	2140	1426
.312	455	9.16	2.88	3830	162.0	881	2110	1229
.312	503	8.28	2.47	3285	149.0	1040	2140	1100
.312	543	7.67	2.21	2939	140.0	1180	2140	960
.312	581	7.17	1.99	2647	132.5	1320	2320	1000
.429	415	14.0	4.61	6131	207.5	535	2550	2015
.429	456	12.7	3.99	5307	192.0	626	2520	1894
.429	504	11.5	3.43	4562	177.0	737	2580	1843
.429	543	10.7	3.08	4096	167.5	873	2520	1647
.429	581	10.0	2.80	3724	160.0	904	2610	1706
.720	422	23.8	7.76	10320			3250	
.720	452	22.0	6.93	9217			3280	
.720	507	19.9	5.93	7887	239.5	401	3220	2819
.720	549	18.3	5.23	6956	223.0	463	3220	2757
.720	585	17.2	4.77	6344	211.0	518	3250	2732

* International Critical Tables, Vol. III, p. 206.

of 5 percent. The decay constant, β, is given by the slope of this curve and a typical curve for determining β is shown in Fig. 8. The experimental values of β determined by the above method are shown in column 8 of Table I. When these values of β, at constant temperature, are plotted against vapor pressure the resulting curves are similar to those obtained by Zemansky.[2]

It is of interest to compare these experimental values of β with those to be expected when the values of the equivalent absorption coefficient of mercury vapor to resonance radiation, as calculated on the basis of Kenty's theory, are used in Milne's[6] theory of radiation diffusion. It has been shown by Milne[6] that

$$\beta=(1/\tau)/[1+(\bar{k}L/\lambda_1)^2], \qquad (1)$$

[6] E. A. Milne, J. Lond. Math. Soc. **1**, 1 (1926).

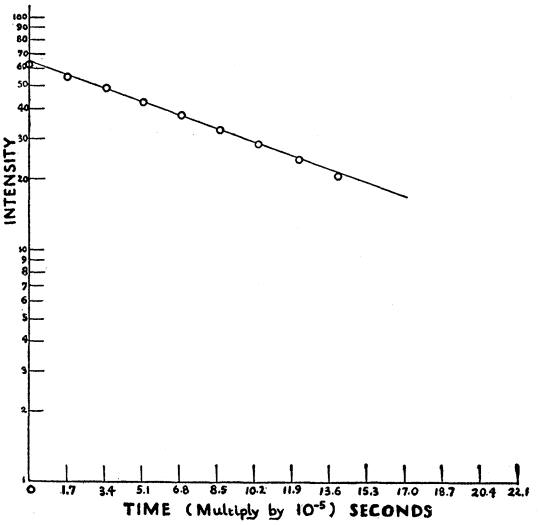


FIG. 8. Curve showing logarithm of intensity of afterglow as a function of time in seconds after cut-off.

where τ is the lifetime of the excited state, $\bar{k}$ is the equivalent absorption coefficient, L is the thickness of the slab of mercury and λ_1 is the first root of the equation

$$\tan y=\bar{k}L/y. \qquad (2)$$

Zemansky[5] has calculated values of the equivalent absorption coefficient on the basis of Kenty's theory for various values of k_0L where k_0 is the absorption coefficient for the center of the line. In the calculations[7] it is necessary to compute the Doppler breadth of the radiation from the equation

$$\Delta\nu_D=5.97\times10^7T^{\frac{1}{2}}. \qquad (3)$$

Values of k_0L were then obtained from the equation[8]

$$k_0L=1.33\times10^{-4}NL/\Delta\nu_D, \qquad (4)$$

where N is the number of molecules per cc.

Values of k_0L obtained in this way are shown in column 5 of Table I. Corresponding values of $\bar{k}L$ were obtained[9] from a plot of Kenty's equivalent opacity as a function of k_0L and are listed in column 6 of Fig. 1. The theoretical

[7] For further details see Mitchell and Zemansky, *Resonance Radiation and Excited Atoms.*

[8] Reference 7, pp. 100 Eq. (35) or Eq. (3) of a paper by M. W. Zemansky, Phys. Rev. **36**, 219 (1930). The numerical coefficient in the latter case is different from that in Eq. (3) and reference 7 due to the use of a probably less accurate value of τ.

[9] See reference 7, pp. 331.

values of β from Eq. (1) are listed in column 7 and the differences between such theoretical values and the experimental results are listed in column 9.

It is quite apparent from an examination of columns 7 and 8 that the disagreement noted by Zemansky between the predictions of Kenty's theory and his results at the higher vapor pressures become increasingly greater as the vapor pressure is further increased. At the highest vapor pressure the theoretical and experimental values are of an entirely different order of magnitude.

It has been suggested that this deviation might be due to Holtsmark broadening. On the basis of Weisskopf's[10] theory the Holtsmark broadening should vary linearly with P/T. Because of such increased broadening at the higher pressures one would expect $\bar{k}L$ to have larger values than are calculated on the basis of Kenty's theory so that β should increase with pressure. On the other hand one might expect that due to Holtsmark broadening alone β should decrease with increasing temperature at constant pressure due to the lowering of the density to maintain constant pressure. This may be the reason for the fact that the experimental value of β decreases with increasing temperatures for pressures of 0.151 mm and above. In this same region of pressure (0.151 mm–0.312 mm) the value of β at a given temperature decreases with increase in pressure, a result difficult to reconcile with the expected effect of Holtsmark broadening. The observations at higher pressure (0.429 mm and 0.720 mm) on the other hand do show a decrease with increase in pressure for the same temperature.

The results obtained at the lowest pressure, namely, an increase in β with rise in temperature is in marked contrast with the results obtained at higher pressures. Heretofore experiments of this kind on pure mercury vapor have been conducted in such a manner that in the main the pressure only has been varied. When attempts[4] have in the past been made to explain the results of such experiments on the basis of Kenty's theory it has been assumed that differences corresponding to column 9 Table I may be due to the presence of Holtsmark or other broadening. The results of the lowest pressure are of such a nature that it is extremely difficult on present theories to understand how such broadening can be alone responsible for these discrepancies.

In Zemansky's earlier theory and later in the work of Kenty,[4] the suggestion has been made that the rise in the value of β beyond the minimum in $\beta-P$ curves may be due to quenching of the excited state. Inasmuch as the number of collisions at constant pressure varies as $T^{-\frac{1}{2}}$ it is difficult to associate the marked increase of β with temperature at the lowest pressure (and for the highest temperature for some of the other pressures) with quenching unless the efficiency of this process is a markedly increasing function of temperature.

No doubt the phenomena are complex and the present experiments indicate additional difficulties for present theories. The complete explanation must await a detailed calculation of the effect of Holtsmark broadening on the equivalent absorption coefficient. There is of course the possibility that the results at the lower pressure may finally be accounted for by a combination of Kenty's theory and Zemansky's metastable atom theory. We hope soon to undertake similar observations as herein reported with the same and a thinner resonance cell over the region of lower vapor pressures.

[10] V. Weisskopf, Phys. Zeits. **34**, 1 (1933).

FIG. 5. Photograph of density marks and afterglow.

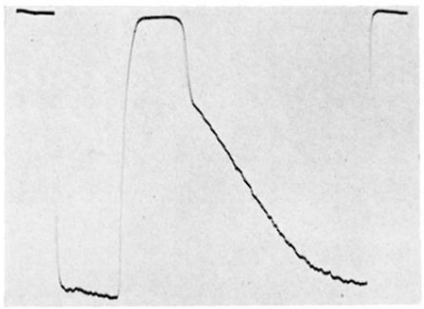


FIG. 6. Microphotometer trace of afterglow.

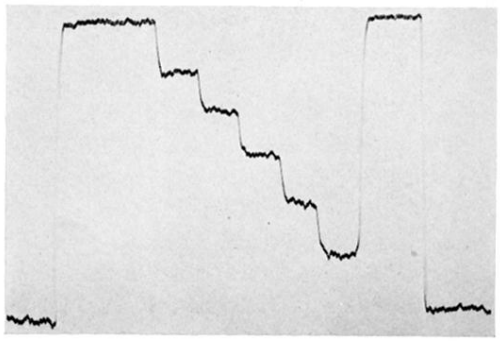


FIG. 7. Microphotometer trace of density marks.