THE METASTABLE STATE IN MERCURY VAPOR

By Harold W. Webb

Abstract

Metastable state produced in mercury vapor at low pressures by electron impacts of 4.9 volts.—The persistence of the "radiation" produced by 4.9 volt impacts in mercury vapor was measured in a four electrode tube of the type usually employed in resonance potential measurements, consisting of an *equipotential cathode of simple design*, an inner grid G for controlling the velocity of the impacting electrons, an outer photo-electric grid H and a photo-electric plate P. A.c. and d.c. voltages were applied to the two grids in such a way that the electrons had sufficient velocity to excite the radiation only in alternate half-cycles and that the photo-electric current to the electrometer alternated in direction simultaneously. As a result of the persistence of the radiation there resulted a decrease in the current with increasing frequency, reaching a minimum at 1800 cycles for a distance between grids of 17 mm and at 3800 cycles for a distance of 8.5 mm. These results did not vary much with pressure, .003 to .032 mm. They show a lapse of time between the excitation and the arrival of the first radiation at the plate P of about 1/3600 and 1/7600 sec. respectively. A mathematical discussion shows that the diffusion of the radiation by repeated emission and re-absorption (the "imprisonment" of radiation theory) cannot account for these results. A calculation, based on the assumption that the excited atoms remain in a metastable state and carry the energy of excitation to the photo-electric surfaces and there give it up, gives results in very close agreement with the observations. The conclusion is that a metastable state is formed by the atoms excited by the 4.9 volt electron impacts and that these are the effective ones in producing the photo-electric response in the tubes. In these experiments the $2p_2$ state is the only one excited by the impacts in appreciable amount. How these results can be reconciled with the *Bohr theory*, according to which the $2p_2$ state is not metastable, is not clear.

Introduction

THE time τ during which an electron displaced to an outer orbit of an atom, either by the absorption of a quantum of the corresponding wave-length or as the result of an electron impact, remains there, has been studied by many methods and has been the subject of much speculation.[1] A knowledge of this time of excitation is important in the study of the absorption by a gas or vapor of lines of the series converging at the orbit of the excitation, since such absorption depends upon the concentration of the partially ionized or "excited" atoms in this state of excitation. The phenomena of low voltage arcs can apparently be explained only by cumulative excitation, that is by successive electron impacts or bythe

[1] Foote and Mohler, The Origin of Spectra, Chaps. IV, VI.

addition of electron impacts and the absorption of radiation, both of which require a long life for the radiation or the excited atoms in the mass of vapor.[2] The experiments with "impacts of the second type," in which the energy of excitation of mercury atoms in the $2p$ state is transferred to atoms of other vapors also depends upon the concentration of the atoms in the $2p$ state and consequently on the time τ.[3]

The value of τ for $H\alpha$, $H\beta$ and $H\gamma$ has been measured with considerable care by Wien[4] and Dempster,[5] who found values for the time constant of the radiation, which decayed exponentially, lying between 2 and 5×10^{-8} sec. Attempts to measure directly the duration of the excited state $2p_2$ in a mercury atom, produced by absorption of $1S-2p_2$ (λ2536.7), by observing the spread of the fluorescent beam due to a transverse stream of mercury vapor, gave negative results, indicating a very short life for the excitation (10^{-6} seconds or less).[6] Indirect measurements of τ have been made by observing the extinction of fluorescence by the addition of other gases, oxygen, helium, etc. The calculation of τ was based on the assumption that each impact between an excited mercury atom and a foreign molecule resulted in the destruction of the radiation. From the probability of impact and the pressure of the foreign gas at which the fluorescence disappeared, a value of τ lying between 10^{-7} and 10^{-8} sec. was computed. Similar experiments on the rate of dissociation of hydrogen by the excited mercury vapor lead to the same result.[7] In all of these experiments the effective radius of the atom is an unknown and fundamental factor in the calculations. Experiments by Wood[8] with moving vapor excited to fluorescence, have shown that the emission of the fluorescent radiation begins 1/15000 to 1/40000 sec. after the excitation of the vapor, a phenomenon which is, however, probably associated with a more complex form of mercury than the atom.

To explain the high concentration of excited atoms in the $2p_2$ state necessary for the action of the low voltage arc, K. T. Compton and others have assumed that the radiation suffers "imprisonment."[9] In this theory radiation follows excitation after a time τ, equal approximately to 10^{-8} sec. Absorption follows immediately, and by repeated absorption and re-

[2] K. T. Compton, Phys. Rev. **20,** 283 (1922)
[3] Klein and Rosseland, Zeit. f. Phys. **4,** 46 (1921)
Cario and Franck, Zeit. f. Phys. **17,** 202 (1923)
[4] W. Wien, Ann. der Phys. **66,** 229 (1921)
[5] Dempster, Phys. Rev. **15,** 138 (1920)
[6] Stern and Vollmer, Phys. Zeit. **20,** 183 (1919)
[7] Cario and Franck, Zeit. f. Phys. **11,** 161 (1922)
[8] Wood, Proc. Roy. Soc. **99,** 362 (1921)
[9] K. T. Compton, l. c.[2]

emission the quantum of radiation diffuses through the vapor. The duration of the radiation in the vapor is therefore equal to $n\tau$ where n is the average number of absorption and radiation processes experienced by each quantum. This "imprisonment" of radiation has also been assumed in the study of absorption and of impacts of the "second type."

Horton and Davies[10] have observed radiation excited in helium and hydrogen to pass through the vapor around a U-tube, and have also explained this by "imprisonment" of radiation, and its "diffusion" through the gas. On the other hand, recent experiments by Kannenstine[11] on the striking conditions of the low voltage arc in helium have shown a long persistence of the excited state in the atom and indicate that a metastable state $2s$ in the orthohelium series accounts for the persistence, which is of the order of several hundredths of a second.

The experiments described in this paper were made to determine the life of the radiation in mercury vapor, excited by electron impacts rather than by fluorescent absorption. Sufficient voltage was used to displace the valence electron to the $2p_2$ orbit. By this method of excitation it was expected that some of the complications met with in the fluorescence experiments would be avoided. The use of a direct method of measuring the persistence of the radiation emerging from the vapor was devised to lessen the difficulties of interpretation.

Method

The mercury vapor was contained in a four-electrode tube, consisting of a hot cathode F, accelerating grid G, a photo-electric grid H and a photo-electric plate P, similar to the tubes used in the ordinary ionization and radiation potential measurements. The "excitation system," F-G, and the detecting or "photo-electric system," H-P, were separated electrically by suitable distributions of voltage. An alternating voltage was impressed between F and G, so arranged that during the positive half-cycle the electrons were given velocities sufficient to give 4.86 volts ($1S-2p_2$) excitation to the mercury atom, while during the negative half-cycle the applied voltage was below this resonance potential. This resulted in an intermittent excitation. Voltages of the same frequency were applied between P and H of the photo-electric system.

The latter system was not unilateral but gave a current from the grid to the plate as well as from the plate. With small frequencies (60 cycles) all the radiation resulting from the electron impacts in a given half-cycle reached the photo-electric surface in the same half-cycle and consequently

[10] Horton and Davies, Phil. Mag. **42,** 746 (1921); **46,** 872 (1923)
[11] Kannenstine, Astrophys. J. **55,** 345 (1922); Phys. Rev. **23,** 108 (1924)

there was a photo-electric current from the plate only. As the frequency was increased, however, owing to the persistence of the radiation in the vapor, some of this radiation reached the photo-electric system in the following negative half-cycle and for higher frequencies was distributed over many following half-cycles. Hence as the frequency increased the "positive" photo-electric current decreased and the "negative" current increased, the resulting electrometer current consequently decreasing. At very high frequencies the electrometer current approached

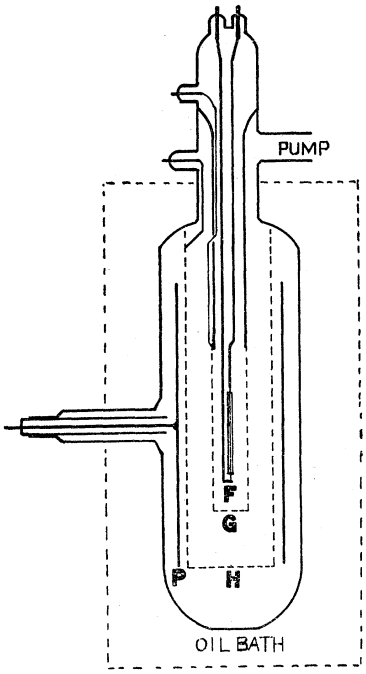


Fig. 1. Tube I.

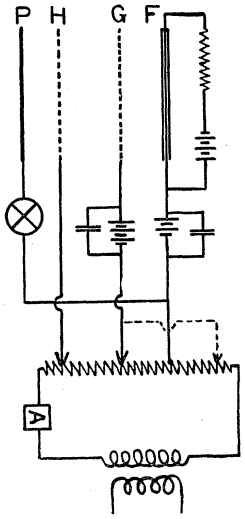


Fig. 2. Electrical connections.

a constant value. From the resulting curves the duration and the law of decay of the radiation produced at any instant by electron impacts, as measured by the part reaching the photo-electric surface, was determined.

Apparatus

Two tubes were used in these tests. For convenience they will be referred to as tubes I and II. Tube I is shown in Fig. 1, the essential parts drawn to scale.

The equipotential cathode *F* consisted of a heater, a strip of platinum $2.5\times0.3\times.0025$ cm, carrying a current of from 3 to 4 amperes, and an

equipotential sheath of platinum, .0025 cm thick, folded closely around the heater with a thin layer of mica between for insulation. Before mounting, the whole was pressed together to insure good thermal contact. This form of equipotential cathode gave little trouble as regards insulation or warping, was easy to construct and had good electrical efficiency. A coating of barium and strontium oxide was used. The emission was from .0001 to .001 amp. The grids G and H were of nickel gauze, 1.6 mm spacing, both being in the form of cylinders closed at the lower ends. Their dimensions were 1.3 cm diam. $\times$ 5.0 cm length, and 3.0 cm diam. $\times$ 15.0 cm length, respectively. The photo-electric cylinder P (3.8 cm diam. $\times$ 10.0 cm length) was of polished nickel sheet supported on an insulating quartz tube through which the electrometer connection passed. A small quantity of liquid mercury was placed in the bottom of the tube.

Tube II was similar to this except that all the essential dimensions of the electrodes except their length were doubled. Oxidized copper gauze was used in place of nickel.

The temperature of each of the tubes was held constant by a surrounding oil-bath, controlled thermostatically. The pumping system consisted of an oil and a mercury diffusion pump with MacLeod gauge. In all the tests described the tubes were pumped until the gauge indicated the pressure of the residual gas to be .0001 mm or less. The pumping was continued throughout the tests. The photo-electric currents were measured on a Dolazalek electrometer (sensitivity 1500 mm per volt) shunted by adjustable capacities.

Dry batteries were used to give the d.c. potentials to the various electrodes. The sources of a.c. were the 60 cycle lighting circuit and a vacuum tube oscillator (output 5 watts). The a.c. potentials (Fig. 2) were applied to the experimental tube by a circuit coupled alternately to these two sources and containing a non-inductive potentiometer resistance from which the desired voltages were taken, a hot-wire meter and a rheostat for adjusting the current. The potentiometer resistances were very small compared with the impedances between the corresponding parts of the experimental tube. For high frequencies fine straight wires were used for which the high and low frequency resistances were practically equal, and the circuit was tuned by a variable condenser. Condensers were used as filters to eliminate high frequency components in many of the tests. By-pass condensers were placed in parallel with the dry batteries used in the circuits.

The frequencies were measured with a wave-meter or by comparison with known sound frequencies.

Experimental Results

D.c. characteristics. For each tube a careful study was made of the d.c. characteristics of both the excitation and the photo-electric systems. Figs. 3(a) and 3(b) show the electrometer current as a function of the voltage $G-F$ for tubes I and II, respectively. In these tests the following voltages were used, $P=0$, $H=3$, $F=2\frac{1}{2}$ and G variable. The points of interest are a small threshold current, due to leakage or the light from the filament, a

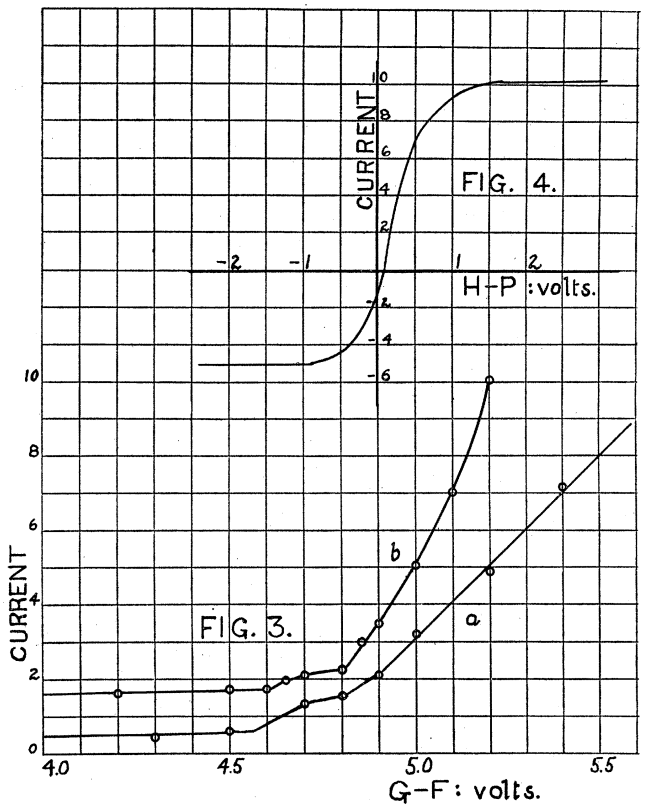


Fig. 3. Electrometer current as function of voltage for tubes I and II.
Fig. 4. D.c. characteristics of the photo-electric system.

small break at 4.7 volts and a marked break at 4.9 volts.[12] (A correction of a few tenths of a volt is usually necessary on these curves.) Other breaks at higher voltages were observed but are not here recorded.

A typical curve of the d.c. characteristics of the photo-electric system is shown in Fig. 4. The voltages $G-F$ and $G-H$ were here held constant

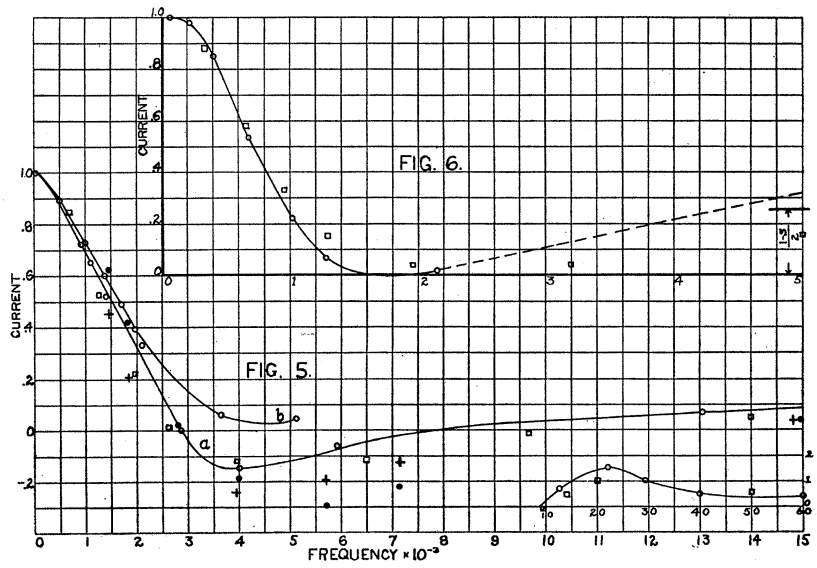
[12] Franck and Einsporn, Zeit. f. Phys. **2**, 18 (1920)

and that of H varied with respect to P. The electrometer current is plotted against the voltage of H. This reverses with reverse of voltage owing to the photo-electrons freed by H, and shows saturation for both negative and positive voltages. The ratio of these saturation currents is an important factor in the measurements and is designated in this paper by S. Owing to changes in the condition of the surfaces this ratio was subject to rapid variations and frequent redeterminations of its value were necessary. Its value varied between 0.1 and 1.8, depending upon the geometry and condition of the surfaces.

Measurements with a.c. To simplify the conditions of excitation the measurements were made with a d.c. potential difference between G and F equal to that of the "4.9 volt" break. This potential was chosen so that an a.c. voltage with a peak value of from 0.3 to 0.6 volts would give negligible excitation in the negative half-cycle and excitation in the positive half-cycle beginning immediately with change in sign of the voltage. The form of the excitation curve in the positive half-cycle as computed from the d.c. excitation characteristics was approximately the same as the positive half of the sine curve, so this approximation was used in computation. As in the d.c. measurements the voltage between F and P was made sufficiently large to prevent the electrons from F reaching P. Positive ions from F were kept back by the positive voltage on G except when this was less than 2 volts above F when large positive currents were observed. The a.c. voltages on the photo-electric system were varied from 1.5 to 3.0 volts and were either in phase with the a.c. of the excitation system or 180° out of phase. The impedances of the circuits involved were such that these phases were not affected more than a few tenths of a degree by the capacity in the tube.

In all the measurements with variable frequency 60 cycles was taken as the reference frequency as it gave the same results as zero frequency, since no measurable radiation reached the photo-electric system in the negative half-cycle. To insure that the amount of excitation was the same at each of the high frequencies as at 60 cycles the currents in the potentiometer were always adjusted to the same value. A further test, made frequently during a determination, consisted in putting a constant potential between H and P and applying a.c. to the excitation system only. The electrometer current was found to be the same within errors of measurement for all frequencies even up to one million cycles, except in certain cases when fluctuations due to high frequency surges or leakage of positive ions occurred. In every such case conditions were varied until the above test indicated proper functioning of the apparatus.

A further fundamental test of the behavior of the system with varying frequency was made at frequent intervals. The voltage $G-F$ was held constant and a.c. applied only to the photo-electric system. The same current was obtained with 60 cycles as with higher frequencies, even up to one million cycles. In making this last test it was found necessary to so alter the connections that the difference of potential between H and G was constant throughout the a.c. cycle. Otherwise the excitation during the positive half-cycle was larger (in some cases 20 percent) than during the negative, owing to the smaller counter field between H and G during the positive half-cycle. With 60 cycles this gave more radiation in the positive half-cycle, while with higher frequencies, owing to the persistence, the radiation reaching the photo-electric plate in each half-cycle was more nearly equal. The resulting difference in the electrometer current could be readily measured.



Figs. 5 and 6. Typical a.c. curves; ratios of higher frequency current to 60 cycle current as a function of frequency.

Results. Figs. 5(a), 5(b), and 6 show typical a.c. curves obtained with the two tubes. The abscissas are frequencies, and the ordinates the ratios of the electrometer currents when these frequencies were applied to G and H to the current with 60 cycles. The curves in Fig. 5 were obtained with tube I, with the following voltages: d.c., $H=P=0$, $F=3.1$, $G=7.8$; a.c., $H=3.0$, $G=0.6$, phase difference, 180°. Curves (a) and (b) were obtained with the tubes at 36°C and 27°C, respectively, corresponding

to pressures .006 and .003 mm. The respective values of S were 1/.85 and 1/.60. The part of curve (a) corresponding to frequencies 10,000 to 60,000 is plotted to a smaller scale in the lower right-hand corner of the figure.

Fig. 6 was obtained with tube II under the following conditions: d.c. voltages, $H=P=0$, $F=6.2$, $G=11.0$; a.c. voltages $H=3.3$, $G=0.4$, in phase; temperature 35°C; pressure .006 mm; $S=0.48$. The observed points are marked with circles on these curves. The dotted portion in Fig. 6 is the estimated extrapolation of the curve for the higher frequencies for which measurements were unfortunately not taken, and is based upon the value for high frequencies, computed from S, and the general form of the curves obtained with tube I.

Discussion

Three important characteristics are noted in these curves. 5(a) and 6 were taken with two similar tubes the principal dimensions of which were in the ratio of 1 to 2. If the abscissas of curve 5(a) are reduced by one-half and the ordinates reduced to the same value of S, the two curves become identical within experimental error, showing proportionality to the dimensions. The second point is the minimum in Fig. 5 occurring at 4000 cycles, after which the curve rises to a maximum and then drops again to the calculated limiting value $(1-S)/2$. This minimum was due to a lapse of time between the excitation and the arrival of the first radiation at P. The third point of interest in the curves is their independence of the vapor pressure. Curves (a) and (b), Fig. 5, show the effect of a four-fold change of pressure. Reduced to the same value of S these curves are practically identical. Other tests over a wide range of vapor pressures (25°−70°; .003 mm to .032 mm) under many different conditions resulted in only small changes in the curves.

The interpretation of these curves is somewhat difficult owing to the fact that the electrometer current is the sum of both positive and negative currents. If the energy resulting from the excitation in a certain positive half-cycle of frequency n which reaches the photo-electric system during the same half-cycle be U_1, that during the following negative half-cycle be V_1, and that during the subsequent half-cycles be U_2, V_2, U_3, etc., we have $n(\Sigma U+\Sigma V)=K$, a constant, since the total radiation produced per second is independent of the frequency. The electrometer current is, to a close approximation, proportional to $n(\Sigma U-S\Sigma V)$, if the voltages on G and H are in phase. If out of phase by 180° the reciprocal of S is used in these calculations. For 60 cycles no measureable persistence existed; $V_1=U_2=V_2=\cdots=0$, and the electrometer current was pro-

portional to K. The ordinates of the above curves are then equal to $n(\Sigma U - S\Sigma V)/n(\Sigma U + \Sigma V)$. The limiting value of this ratio for high frequencies is $(1-S)/2$, since $\Sigma U = \Sigma V$ in the limit.

Imprisonment theory. The persistence of the radiation in the vapor may be explained either by the formation of a metastable state or by the "imprisonment of radiation," in which latter process the radiation is handed on from atom to atom by repeated absorption and re-emission. The results to be expected on the imprisonment theory were calculated as follows. Assuming that the radiation "diffuses" in a cylindrical mass of vapor of radius R, passing from atom to atom without any preferred direction, we have the following differential equation for E, the density of the radiation;

$$\frac{\partial E}{\partial t} = a^2\left(\frac{\partial^2 E}{\partial r^2} + \frac{1}{r}\frac{\partial E}{\partial r} + \frac{\partial^2 E}{\partial z^2}\right).$$

The constant a^2 depends upon the absorptive properties of the vapor for the radiation in question, and t, r and z have the usual meanings. No account is here taken of the dissipative absorption, since the data on absorption are not available and these computations are made only to determine limiting values. The solution of the equation, if we assume for a first approximation that the problem is independent of z, is

$$E = \Sigma A_m e^{-\mu^2_m a^2 t} J_0(\mu_m r), \tag{1}$$

where μ_m is a root of the equation $J_0(\mu R) = 0$, since the density of radiation is zero at the surface of the cylinder, if we neglect reflection. The distribution of the electron impacts producing radiation may be closely represented in space and time for one half-cycle by $f(r)F(t)$, where $f(r)$ is zero for all values of r except in the region of the inner grid, where it may be assumed constant and equal to unity, and, approximately, $F(t) = \sin 2\pi n t$ from $t=0$ to $t=1/2n$, and is zero for all other values of t, n being the frequency. We have $f(r) = \Sigma A_m J_0(\mu_m r)$. For $t=0$ to $t=1/2n$,

$$E = \int_0^t f(r)F(t)e^{-\mu^2_m a^2(t-\tau)}d\tau$$
$$= \Sigma A_m J_0(\mu_m r)\ [\mu^2_m a^2 \sin 2\pi n t - 2\pi n \cos 2\pi n t + 2\ n\ e^{-\mu^2_m a^2 t}]/B$$

and for later times

$$E = \Sigma A_m J_0(\mu_m r)\ [2\pi n(1+e^{-\mu^2_m a^2/2n})/B]\ e^{-\mu^2_m a^2 t}$$

where $B = \mu^4_m a^4 + 4\pi^2 n^2$.

The rate of transmission of the radiation to the walls is given by $-a^2 \partial E/\partial r$ for $r=R$. Multiplying by $\mu^2 a^2 \pi n$ to reduce to equal rate of production of radiation, integrating the electrometer current separately

over each half-cycle and combining the terms, we find for the electrometer current, using S as above,

$$C = \Sigma A_m J_1(\mu_m R)\mu_m \frac{[\mu_m{}^4 a^4 + 2\pi^2 n^2 (1-S)]}{\mu_m{}^4 a^4 + 4\pi^2 n^2}.$$

This series converges very slowly and it is not easy to compute the value of C for each frequency. For estimating a maximum value of a^2 we can take the first term only. The value of $\mu_1{}^2 a^2$, which best fits the curve in Fig. 6 (tube II) is 4000 sec.$^{-1}$ Now $\mu_1 = 2.4/R$, giving $a^2 = 10000$ for $R = 3.8$ cm. Assuming the radiation to diffuse in a manner similar to the atoms in a gas, we have $a^2 = \lambda c/3$ where λ is the "mean free path" of the radiation between atoms and c is its mean "velocity." The actual time of passage of the radiation between atoms is negligible, but the length of each absorption and radiation process is τ. Hence $a^2 = \lambda^2/3\tau$. If τ be 2×10^{-8} sec. we find $\lambda = 0.2$ mm, or, if we take $R = 2(3.8)$cm to allow for the approximations made in regard to the z coordinate and reflection at the walls, $\lambda = 0.4$ mm. This is its maximum possible value on the imprisonment theory. Since the later terms in the series are large the actual value is probably much smaller. If λ is inversely proportional to the vapor pressure, as we might expect by analogy with the free path of atoms in gases, the exponents $a^2\mu^2$ in the above expressions will change inversely as the square of the pressure, and we should expect the corresponding times to be proportional to this square. Again since in Eq. (1) μ varies inversely as R, the exponential terms $\mu^2 a^2 t$ require, for two tubes geometrically similar, the corresponding times to be proportional to the square of the dimensions. Neither of these relations was observed, as already pointed out.

Metastable state. These considerations and studies made of the distribution of the radiation produced in a mass of mercury vapor by electron impacts, lead to the conclusion that the persistence of the excited states involved in these experiments is the result of the formation of metastable states. The diffusion of radiation throughout the apparatus must therefore depend largely upon the diffusion of the excited atoms. The curves show that the time between the excitation and the arrival of the radiation at the photo-electric surfaces was proportional to the first power of the dimensions and was of the same order of magnitude as the time required by an atom having the mean velocity corresponding to the temperature of the vapor to pass across to the photo-electric system. In the case of tube II discussed above, the radius was 3.8 cm and the mean velocity of the mercury atoms was 2×10^4 cm/sec., so that the average time of transit of a metastable excited atom to the walls would have

been of the order of 1/5000 sec. The value of the exponential constant found assuming the radiation in the vapor to decay exponentially was 4000, giving the time constant as 1/4000 sec. which agrees well with the above average time.

The following calculation was therefore made, applying to tubes I and II. It was assumed that the "radiation" was carried to the photo-electric system by the excited atoms and given up either by impact on the surfaces or when very close to them. The shortest distance from the region of excitation, which was close to the inner grid G, was along the radius, approximately equal to two-thirds the radius of the cylinder P. This distance we shall call D. If all the excited atoms followed this path without impact the photo-electric action resulting from the electron excitation $Id\tau$, produced in any interval $d\tau$ at time τ, would be given by the expression

$$GIe^{-hmD^2/(t-\tau)^2}[1/(t-\tau)^4]d\tau,$$

where G is a constant and h and m are the constants of kinetic theory. This takes into account only the velocity distribution and the path. By a graphical integration the photo-electric excitation resulting from the excitation produced in one whole positive half-cycle was determined as a function of the time, and from this the electrometer current resulting from the alternating voltage on H was determined for the frequency range involved in the experiments.

Since all directions of motion are possible for the excited atoms it is necessary to consider also those taking the longer paths to the photo-electric system. Assuming no impacts to occur the probable distribution of the atoms among the possible paths, which varied in length between D and $5D$, was computed, allowing for the shadowing of the inner grid, etc. The above calculation was again made taking into account all these paths and the relative number following each. Using two-thirds the radius of P as the value of D, 1.3 cm for tube I, the values marked by crosses on Fig. 5 (a) were obtained, which agree roughly with the experimental curve. The effect of impacts by the excited atoms was also calculated on the assumption that impacts result in dissipation or in radiation which does not reach the photo-electric surfaces. Using the free path as for the unexcited atom for vapor at 30° the values marked by solid circles were found. For the higher temperature actually used to obtain curve (a) the values computed depart a little further from the curve in a manner indicated by these two sets of points.

A better agreement for the pressure .006 mm, corresponding to the temperature 35° at which the curve in Fig. 5(a) was taken, is obtained

if we assume that impacts do not result in dissipation of the excitation but that the atom continues in the excited state. The mean free path was 0.45 cm, roughly $D/2$. A series of rough approximations gave the distribution of the excited atoms after each impact assuming that each traversed the full mean free path between impacts. The error in this calculation is large but the results are sufficiently close for our purposes. The distances traveled by the different atoms before reaching the walls was then found. The curve computed for this distribution of paths is marked by squares on the figure, and shows that this assumption fits the observations as well as can be expected. This same curve has been plotted on Fig. 6, also marked by squares, by taking the dimensions of tube II and the value of S used and recomputing without taking into account the fact that the free path was there $D/4$. This has been done to show the similarity of the two curves and the proportionality of the times involved to the dimensions.

The approximate nature of the above computations and the uncertainty of the exact conditions obtaining as well as the probability that other processes are involved makes it uncertain as to how far we may go in drawing conclusions from the rather remarkable agreement between the computed and observed curves. The dimensions of the tube are not known to better than 15 per cent, and the pressures are probably not as large as calculated from the temperatures, owing to the condensation in the neck of the tube and the high temperature in the neighborhood of the filament. A number of other possible factors suggest themselves, such as the transfer of the excitation at impact, radiation and reabsorption, selective as regards the velocity of the absorber, high dissipative absorption, and a probable difference in the sensitivity of different parts of the photo-electric surfaces. The agreement between the calculated and observed curves is, however, significant in two respects. The close agreement in the first part of the curve on the positive side of the axis shows quite conclusively that the velocity of the atoms is the determining factor in the rate of travel of the excitation energy and leads to the conclusion that we are dealing here with a metastable state of rather long life. The agreement of the calculated curves with the observed as regards their form, both showing a minimum at about 4000 cycles and a maximum at about 20,000 cycles, and both coming to the same final value at about 50,000 cycles bears out the same conclusion.

The outstanding difficulty in the interpretation of these results is the apparent lack of dependence on the vapor pressure. Assuming that the true pressures are as given by the temperatures the curves should show more difference than was observed as the pressure was varied. This

might be explained on the assumption that the excitation energy is transferred from atom to atom on impact, the probability of such a transfer depending upon the directness of the impact, being greatest for head-on collisions. This would result in an added persistence of velocity at impact and would diminish the effect of impacts on the total paths and the time required for the excited atoms to reach the photo-electric system. Other assumptions suggest themselves but the results do not differentiate between them sufficiently to justify further discussion.

In these experiments we have to deal with the result of exciting atoms in the $2p_2$ state with a negligible number of atoms excited initially in the $2p_3$ state. The $2p_1$ state (5.4 volts) was not present. The resonance potential curves (Fig. 3, a, b.) show some $2p_3$ excitation but the amount is small compared with the amount of the $2p_2$ excitation. Furthermore H. Sponer[13] has shown that the amount of $2p_3$ excitation decreases rapidly as the voltage increases above 4.9 volts. This is further borne out by the fact that the "radiation" studied was practically homogeneous as regards life. The frequency-current curves do not indicate the presence of two types of radiation of markedly different persistence, and certainly no measurable quantity of excitation resulting in immediate photo-electric action.

The Bohr theory, however, indicates that the metastable state observed is not the $2p_2$ state since on this theory only the $2p_1$ and $2p_3$ states should be metastable, the transitions $1S-2p_1$ and $1S-2p_3$ not being observed spectroscopically. The $2p_2$ state would not be expected to have a very different degree of stability from that observed for hydrogen and other atoms, 10^{-7} to 10^{-8} seconds. On this theory these results would be interpreted as due to atoms originally excited in the $2p_2$ state and changing, at least in part, to the $2p_3$ state, in which state they carry the energy across to the photo-electric surfaces, no measurable number of the atoms in the $2p_2$ state being effective. There is, however, some ground for looking also for a metastable $2p_2$ state, although the evidence is meager. The work of Kurth[14] and others and experiments made here show that excited vapor absorbs and scatters the lines $2p_2$ *-md* to the same degree as the lines $2p_1$ *-md* and $2p_3$ *-md*. If the primary excitation of atoms is principally in the $2p_2$ state and the other states result from this, possibly as the result of atomic impacts, we must assume the average life of the $2p_2$ state in the vapor to be of the same order of magnitude as that of the $2p_3$ state, unless the transformation from the first of these states to the second occurs for only a very small fraction of the atoms.

[13] H. Sponer, Zeit. f. Phys. **7**, 185 (1921)
[14] Kurth, Phys. Rev. **22**, 202 (1923)

If the $2p_2$ state be not also metastable we must assume the process of imprisonment to be effective in order to account for this life. This would result in the present experiments in a somewhat different relation for the rate of arrival of the carriers of the excitation at the photo-electric surface and should further show the effect of the change in the life of the $2p_2$ state with pressure. The evidence is, however, not complete enough to more than suggest the possibility of all three of the $2p$ states being metastable under certain conditions.

The above calculations are inconclusive as regards the cause of the breaking down of the metastable state and the production of the photo-electric action. This breaking down may be (a) spontaneous, (b) due to atomic impacts, or (c) to impacts on the solid walls, etc. For large absorption of radiation only those atoms producing radiation when very near the surface would be effective, so that the results can not differentiate between these possibilities. For smaller absorption the relations are complicated and cannot be readily calculated. It seems probable, however, that impact on the walls accounts for the transformation into photo-electric energy.[15]

Although in these experiments the process involved in the imprisonment theory plays only a small part, it undoubtedly plays some part in the transfer of energy. This is indicated by the results obtained in a study of the mercury arc made in this laboratory, the details of which will be published later. Mercury vapor contained in a quartz cell was excited by the radiation from a separate mercury arc, which was operated intermittently by a commutator. The direct radiation from the arc was tested and found to die out very rapidly. When the cell was interposed between the arc and the spectrograph, the timing device showed that the radiation of wave-length 2536.7 coming from the cell persisted a considerable time after the extinction of the arc, the rate of decay being given roughly by the fact that the intensity of this persistent radiation fell to half value in the time required for an atom having the mean velocity corresponding to the temperature of the cell to traverse one half the length of the cell, a correspondence between atomic velocities and rate of transmission of the radiation which is again very striking. The experiment was made with two cells of different length with similar results. If we consider the mercury in the cell as forming an outer layer surrounding the arc, it is seen that in this case the transfer of radiant energy involved the process of emission and re-absorption, since convection was impossible between the two parts of the apparatus. We must

[15] Schottky, Phys. Zeit. **24**, 350 (1923)

therefore consider the part played by the imprisonment process in a complete explanation of these phenomena.

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