PERSISTENCE OF λ2537 IN MERCURY AT LOW PRESSURES

By Harold W. Webb and Helen A. Messenger

Abstract

The persistence of λ2537 excited by electron impact in mercury vapor was measured for vapor pressures corresponding to the temperature range 78° to −19°C, using the alternating potential method previously described by one of the authors. Between 78° and 17°C this persistence was found to vary inversely as the first power of the pressure, and not inversely as the square of the pressure as predicted by theories of the diffusion of radiation by repeated absorption and re-emission. A modified theory of diffusion of radiation seems necessary to explain the persistence which is much too small to be explained as depending upon the life of the metastable atoms. As the pressure is lowered the persistence approaches a limiting value of the order of 10^{-7} seconds.

The life of λ1849 was found to be less than 3×10^{-9} seconds. A radiation process probably associated with the 7.1 break in the critical potential curves was found to have a life of 1/470000 seconds. It is suggested that this is the life of an infra-red transition to the 6.7 volt level, followed by the radiation of 1849. Another process associated with an excitation potential lying between 5 and 6 volts had a life of about 1/120000 second.

IT HAS been shown by one of the authors[1] that with a modified Lenard tube having a nickel or aluminum photoelectric plate and a quartz filter separating the excitation and detecting systems, the critical potential curves of mercury are due to radiations of wave-lengths less than 2700 and greater than 1650A. The quartz filter eliminated the "photoelectric" effect of the metastable atoms which with the surfaces used was much greater than the true photoelectric effect due to radiation. The radiations detected were as follows: (a) 2537A, (b) 1849A, (c) radiation of wave-length between 2500 and 2200A, probably the molecular band 2338-2313A, and (d) radiation of wave-length between 2200 and 1650A, probably the molecular band 2140A. The other radiations excited below the ionization potential do not directly affect the plate photoelectrically as they lie well above its photoelectric long wave-length limit.

In the present experiments the radiations associated with the critical potential curves were studied further as regards their persistence after excitation. In particular the persistence of 2537 was measured for vapor pressures corresponding to the temperature range 78° to −19°C. The presistence of this line for pressures corresponding to the temperature range 130° to 60°C had already been carefully studied by Zemansky.[2] By means of a rotating sectored disk he intermittently illuminated with 2537 the

[1] Helen A. Messenger, Phys. Rev. **28**, 962 (1926).

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

front face of a quartz cell containing mercury vapor and by a second synchronous disk measured the emission of this line from the rear face as a function of the time after the illumination was cut off. His results did not agree with the simple theory of diffusion of radiation by repeated absorption and re-emission, which has been developed in detail by Milne,[3] and he attempted to account for this by dissipative impacts. In particular the diffusion theory predicts a law of decay of the persistent radiation transmitted by the cell which is roughly exponential, with a constant inversely proportional to the square of the vapor pressure, while Zemansky found that, even at the lowest temperature at which he could make measurements (60°C), this constant varied very much less rapidly.

The method here employed for the measurement of the persistence of radiation is described at length in previous papers.[4] Briefly, this consists

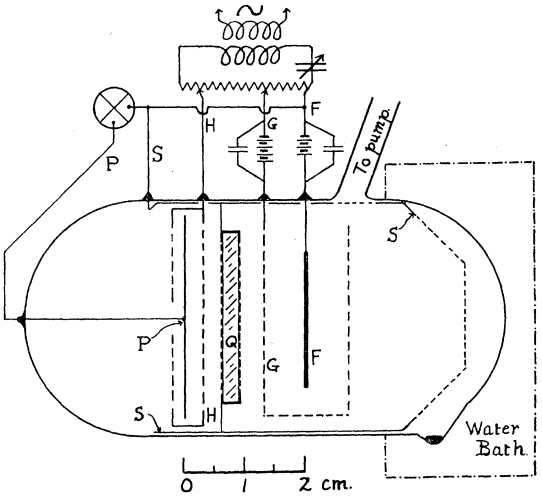

Fig. 1. Experimental tube and electrical circuits.

in exciting the radiation intermittently by applying an alternating potential between the hot cathode F (See Fig. 1.) and the excitation grid G the voltages being so arranged that excitation occurs only in the positive half-cycles. In phase with this is a second alternating potential applied between the detecting photoelectric plate P and the photoelectric grid H which permits photo-electrons to leave P only during the positive half-cycles and causes photo-electrons from H to go to P during the negative half-cycles. As the frequency of the alternating voltages is increased, since the radiation persists after its excitation, it holds over to some extent into the negative half-cycle and the electrometer current from P is reduced. From the variation of this current with the frequency, the persistence may be calculated.

[3] E. A. Milne, Journ. Lon. Math. Soc., No. **1**, (1926).
[4] H. W. Webb, Phys. Rev. **24**, 113, (1924); F. G. Slack, Phys. Rev. **28**, 1 (1926).

Apparatus

The tube used, which was similar to that described by Messenger as Tube I, (Reference 1, p. 964) is shown by diagram in Fig. 1. The oxide-coated hot cathode F was equipotential. The grids G and H were of nickel gauze, as was also the shielding electrode S. The plate was of nickel, polished but not degassed. The quartz window Q separated the excitation and detecting systems, permitting only radiation to pass, and blocking the metastable mercury atoms.

The vapor pressure was controlled by a water bath enclosing one end of the tube, where all the liquid mercury collected. The rest of the tube, including 30 cm of the pumping tube was superheated. To insure having the vapor pressure in the tube that corresponding to the temperature of the bath the pumping tube could be closed by a steel ball seated in a constriction. The bath could be held constant within one degree at temperatures ranging from 80° to -20°C, the low temperatures being obtained by salt and ice mixtures.

During observations a diffusion pump was operated continuously to prevent accumulation of traces of gas, which never exceeded a pressure of 0.0001 mm.

The electrical circuits were similar to those described by Webb.[4] They are shown schematically in Fig. 1. Special care was taken in the design of the oscillators and coupled circuits to insure approximately a sine wave-form for the impressed alternating potentials, as this is essential to the method.

Procedure

The cathode F was held constant at $+4.5$ volts and the shield S and the plate P were at ground potential. The voltage on G measured with respect to F will be described as follows; $G\text{-}F=a\pm b$, a being the fixed potential difference and b the peak value of the superposed alternating potential. The alternating potential used on H was from 3 to 4.5 volts in peak value.

The two tests for proper functioning of the tube and for wave-form described by Webb[4] (Reference 4, pp. 119-120) were used throughout.

With alternating potentials on both systems the ratio of the electrometer currents for high frequency C and for 60 cycles C_0 was determined as a function of the frequency (See Fig. 3.). This ratio R is used instead of the actual current to eliminate variations in emission and plate sensitivity. For all of the times of persistence met with in this work 60 cycles was equivalent to zero frequency, since no appreciable hold-over occurred at this frequency.

If we assume that radiation excited at time $t=0$ falls off according to the law $e^{-t/T}$; if, as was usually the case, the excitation of the radiation varies according to a sine law during the positive half-cycle of the alternating potential on $G\text{-}F$ and is zero in the negative half-cycle; and if the photoelectric current saturates very soon after reversal of the alternating potential $H\text{-}P$,

as was also the case, the current ratio, R, as a function of the frequency f is $R=C/C_0=[(1/T^2)+2\pi^2f^2(1\text{-}S)]\div[(1/T^2)+4\pi^2f^2]$, where S is the ratio of the positive and negative saturation currents of the H-P system for steady radiation. For $f=0$, (60 cycles), $R=R_0=1$. For $f=\infty$, $R=R_\infty=\frac{1}{2}(1\text{-}S)$. Let $R_{1/2}=\frac{1}{2}(R_0\text{-}R_\infty)$ and let $f_{1/2}$ be the corresponding frequency. We have $R_{1/2}=\frac{1}{2}[1+\frac{1}{2}(1\text{-}S)]=[(1/T^2)+2\pi^2f_{1/2}^2\ (1\text{-}S)]\div[(1/T^2)+4\pi^2f_{1/2}^2]$ which gives $1/T=2\pi f_{1/2}$. This gives a simple means of calculating the value of $1/T$ from the "R-frequency" curve. If two radiations with different decay rates are present this relation may be separately applied to the part of the current due to each.

With this method of measuring times of persistence it is difficult to obtain precision unless only a single radiation is effective at one time. It was there-

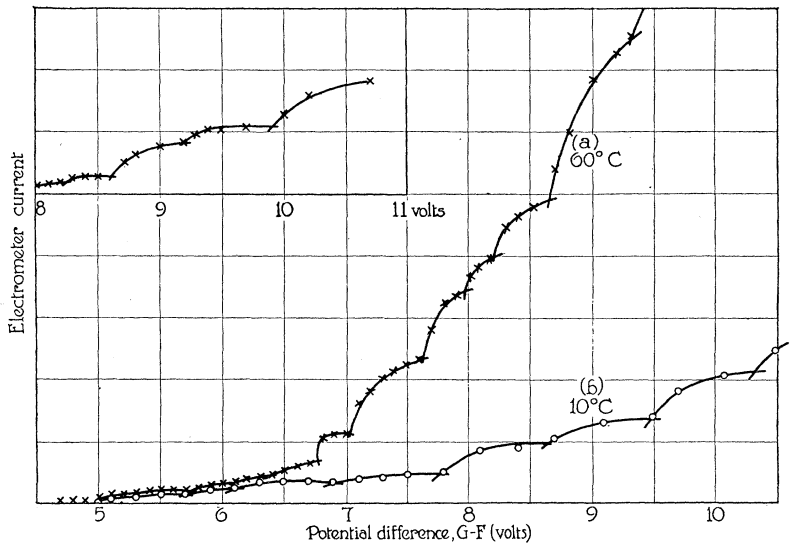

Fig. 2. Critical potential curves with experimental tube at 60° and 10°C. Corrected voltages are given.

fore important to vary the conditions until the radiation to be studied was predominant. This was accomplished in several ways; chiefly, by the variation of the G-F voltages, both fixed and alternating, and by changes in vapor pressure, which in particular had a marked effect on the strength of 2537 relative to that of the other radiations. Again, accidental variations of the plate sensitivity were sometimes a help in separating the radiations. The plate became at times quite insensitive to 2537 and radiations were then measurable which were masked when the plate returned to normal sensitivity.

Results

Fig. 2. shows two ordinary critical potential curves, taken with the tube at 10° and 60°C, respectively. As the quartz window eliminated the metastable atoms, these curves show how the total radiation affecting the plate

varied with the voltage on G. Fig. 3 shows three typical "R-frequency" curves taken with alternating potential on both G and H.

The measurements indicated that there were present in measurable amount four types of radiation. The outstanding one was the line 2537. This radiation is peculiar in that its persistence varies widely with the vapor pressure so that it was easily identified. A second group of radiations of which 1849 probably formed the most important part had a persistence too short to be measured with the apparatus which could not be used with frequencies greater than 3×10^6 cycles. There were found further two other types of radiations having life-times 1/470000 sec. and 1/120000 sec., respectively. Radiations such as 4047, 4358, etc., which are also excited below the ionization potential were not directly effective since the nickel was quite insensitive to wave-lengths greater than 3000A.

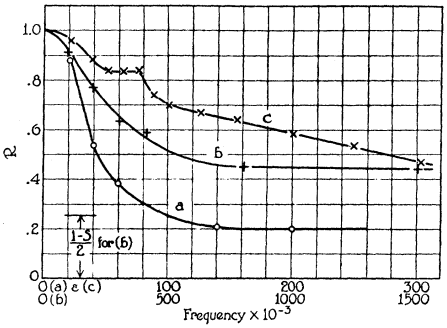

Fig. 3. R-frequency curves. *a*. 40°C, G—$F=5.4\pm1.3$; *b*. 22°C, G—$F=6.7\pm3.3$; *c*. 29°C, G—$F=8.1\pm2.0$.

Wave-length 2537. By trial it was found that the 2537 radiation could be best isolated from the other radiations by using exciting voltages below 6.7 volts. Consequently when possible the curves taken in studying it were with G-$F=5.4\pm1.3$ volts. Measurements of its persistence were made at temperatures covering the range 78° to −19°C. Fig. 3, Curve *a* shows the curve taken at 40°C, illustrating the type of curve obtained.

The assumption made above that the radiation reaching P decays according to the simple exponential expression $e^{-t/T}$ is incorrect if the radiation comes out by any kind of diffusion process. Such a process would be described by an equation the solution of which would contain an infinite series of terms of the exponential form with rapidly increasing negative exponents. The form of the exponents and of the coefficients of the terms would depend upon the geometry of the space in which the diffusion takes place. A solution of the ordinary type of diffusion equation for conditions approximating those in the experimental tube was made and it was found that the corresponding R-frequency curve calculated did not differ greatly from the curve for a simple exponential decay of the radiation. It does not decrease so rapidly at first but the rest of the curve is somewhat steeper than the simpler curve. The difference between the two types of curve is not sufficient, however, to differentiate between them with the present experimental curves. The precision of these is such that an equally good fit can be obtained with either type. Consequently the results of the present measurements are given in terms of $1/T$, the constant in the simple exponential expression computed as described above from $f_{1/2}$. It may be noted, however, that this value is practically equal to the exponential constant in the first term of the series obtained by the solution of the diffusion equation, in the case worked out being too small by about 10 percent.

In Table I, column 3, the values of $1/T$ so obtained from nine curves are summarized. Column 1 gives the corresponding temperatures of the liquid mercury in the tube, while column 2 gives the corresponding number of atoms per cc. Column 4 shows the exciting voltage *G-F*. In the last column appear estimates of precision and other comments.

TABLE I. *Persistence of λ2537.*

Temperature	Number of atoms per cc $\times 10^{-11}$	$1/T$	*G–F* volts	Remarks
−19°C	8.6	(10^7)	6.9 ± 4.6	$6\times10^6 < 1/T < 1.3\times10^7$
−10	26	6.3×10^6	6.7 ± 3.3	Precision 20%
0	77	5.0×10^6	6.7 ± 3.3	" 15%
7	160	2.3×10^6	5.4 ± 1.4	" 15%
17	410	1.3×10^6	5.4 ± 1.3	" 10%; complex curve
22	630	7.5×10^5	6.7 ± 3.3	" 15%; complex curve
40	2000	2.6×10^5	5.4 ± 1.3	" 10%
60	7700	7.9×10^4	5.4 ± 1.3	" 10%
78	22000	2.4×10^4	5.4 ± 1.3	" 15%

It will be noted that at the lower pressures, below 7°C, a higher *G-F* voltage than 5.4 ± 1.4 was used. This was necessary because the low vapor pressure resulted in small excitation. At these pressures the radiations other than 2537 were practically negligible in amount. At −19°C the energy excited was too small for precise measurement. The measurements obtained sufficed, however, to give an estimate of the value of $1/T$ for this pressure of about 10^7 sec^{-1}. At 17° and 22° the curves were each the result of mixed radiation. At 17°, 2537 was mixed with the radiation having the life time 1/120000 sec; at 22° it was mixed with about 25 percent of 1849. (See Fig. 3, curve *b*). The value of $1/T$ for the part due to 2537 was in each case obtained by a graphical analysis of the curve.

These results are plotted in Fig. 4, with $\log_{10}$ concentration as abscissas and $\log_{10}$ $1/T$ as ordinates. The 1000-fold variation in the values of $1/T$ and the 6000-fold variation in concentration make it inconvenient to plot them directly. Opposite each point on the curve is given the corresponding value of the temperature. The dotted portion at the lower right hand part of the figure was obtained by extrapolation from the results of Zemansky.[2] It was assumed that the present apparatus is roughly equivalent to the smaller of his cells which was 1.3 cm thick. This is of the right order of magnitude, as will be seen from Fig. 1. The geometry of the tube is too complex for a more precise computation.

The life of the excited 2^3P_1 state in the mercury atom has been measured by a variety of methods and the value 10^{-7} sec. is the best average of the values found. (Cf Zemansky,[2] p. 519). This life must be the limiting value of the persistence of 2537 as the pressure diminishes and consequently the curve has been drawn asymptotic to this ordinate. The curve indicates that for 10^{11} atoms per cc the time of persistence is practically the life of the excited state and that at this pressure no persistence due to absorption and re-emis-

sion or any similar process delays the radiation in passing to the detecting photoelectric surface.

The curve shows that for no pressure does $1/T$ vary inversely as the square of the concentration of atoms. This would be indicated by a slope parallel to the line CD. The results therefore do not agree with Milne's theory of diffusion of radiation by the process of repeated absorption and re-emission, at least in its simplest form, since this requires $1/T$ inversely proportional to the concentration squared. For the region of concentration corresponding to the temperature range 78° to 17°C, $1/T$ varies very nearly inversely as the first power of the concentration, as indicated by the coincidence of the curve with the 45° line AB.

In spite of the failure of the simple form of the theory of diffusion of radiation to explain the variation of the persistence with concentration, it still seems most probable that for pressures corresponding to temperatures

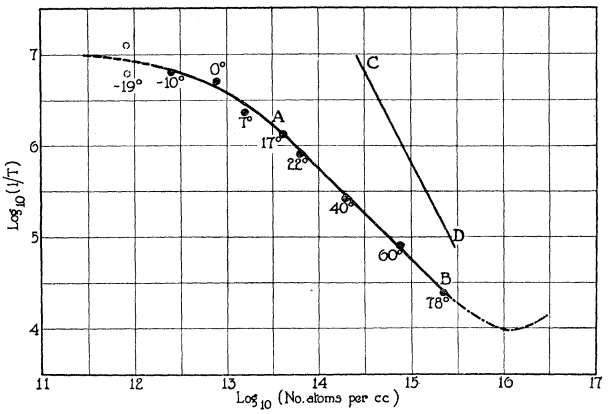

Fig. 4. Persistence of λ2537 vs. concentration.

between 78° and 17°C, we have to deal with a diffusion process consisting of absorption and re-emission. It does not seem possible to explain the persistence in this region as due to the formation of metastable atoms, which carry the excitation energy until as the result of impact they are brought back to the 2^3P_1 state from which they radiate 2537. At 40°, for example, Coulliette[5] has shown that the average life of the metastable atom in the present tube should be of the order of 1/10000 sec., while the average persistence of 2537 actually observed was 1/260000 sec. It may be noted further that at this temperature the interval between impacts is nearly ten times as great as this average persistence of 2537. We can not therefore connect the radiation persistence with the longer lived metastable atoms. Some modified form of the theory of diffusion of radiation by repeated absorption and re-emission seems necessary to explain the present results. It is probable that the present theory fails to describe the facts because it does not take

[5] J. H. Coulliette, Phys. Rev. **32,** 636 (1928).

into account the effect of the breadth of the absorbed line, and of possible processes which may result in the gradual change in the width of the line as the quantum passes from atom to atom. New experiments are in progress to test this directly.

For concentrations corresponding to temperatures below 17°C, the curve deviates from the straight line, as is to be expected since $1/T$ can never exceed the life time of a single excitation which is about 10^{-7} sec. If we regard the persistence as some kind of diffusion process this region corresponds to the condition in which the "mean free path" is nearly equal to or less than the dimensions of the space in which the process is taking place. Under such conditions the diffusion is always slower than is indicated by the diffusion equation as derived for small free paths. For example, at zero degrees we would have on the average only two emission processes and only one absorption of a quantum on its way to P, and we should not expect the ordinary equations of diffusion to apply. For concentrations corresponding to temperatures greater than 78°C the process of persistence is obviously more complex. Zemansky has already discussed the possible causes of this.

From the measurements at 0° and 7° the atomic absorption coefficient was estimated to be of the order of 10^{13}.

Other excitations. When *G-F* voltages with peak values well in excess of 8.3 volts were used the frequency-current curves failed in many cases to drop to the theoretical lower limit $R_\infty = \frac{1}{2}(1\text{-}S)$, even with the highest frequencies available. This was due to the presence of radiation having a life too short to be affected by the frequencies used, estimated as less than 3×10^{-9} sec. From the voltages at which this radiation became prominent it was concluded that it was the line 1849. Eldridge[6] and Messenger (Reference 1, p. 594) both found a rapid increase in the rate of excitation of this line as the exciting voltage increased beyond 8.3 volts. Fig. 3, Curve *b* shows one case in which 1849 is one-fourth as intense as 2537, as measured by the photoelectric current due to each. This curve should eventually fall to $R_\infty = 0.25$, but at $f = 1.5\times10^6$ the part due to 1849 has shown no tendency to decrease.

For *G-F* peak voltages above 7 volts, another type of excitation was found for which $1/T = 470000$ sec.$^{-1}$. The curves showing this were best developed for $G\text{-}F = 5.4 \pm 3.8$ volts. (When the peak voltage considerably exceeded 9.2 volts, 2537 again became very prominent.) The new type of radiation was measured at 60°, 55° and 40°C with practically the same result, so that its life does not depend on the vapor pressure. To determine the minimum voltage at which this radiation is excited the following test was made. With the tube at 60°, and $G\text{-}F = 5.4$ plus a variable alternating voltage of 80000 cycles, and alternating voltage on *H-P*, Curve *a* of Fig. 5 was obtained for the values of R, plotted against peak value of *G-F*. The frequency 80000 was selected since at 60°C the 2537 radiation gives practically $R_\infty = 0.25$, while this 470000 radiation gives the value $R = 0.62$. The

[6] J. A. Eldridge, Phys. Rev. **23,** 685 (1924).

curve, starting at $R=0.27$, increases slowly to 7 volts and then rises rapidly, finally reaching the value 0.62 at 8.3 volts. This is interpreted as follows: 2537 is predominant below 7 volts; at 7 volts the 470000 radiation begins to increase and at 8.3 volts is itself predominant. (The 60° curve for $G\text{-}F=5.4\pm3.8$ shows practically only this radiation.) The slight upward slope of the curve below 7 volts may be accounted for by 1849 which is excited above 6.7 volts. This is confirmed by measurements recorded as the dotted part of the curve which was taken at 500000 cycles for which frequency both 2537 and the 470000 radiation give theoretically $R=0.26$. The difference between this and the observed value is presumably due to 1849.

The point of appearance of the 470000 radiation corresponds closely with the 7.1 break in the critical potential curve. Messenger found that this break was practically absent when these curves were taken through a calcite filter, indicating that part of the radiation associated with this break which is capable of affecting the nickel photoelectric plate lies between 2200 and 1650 and is probably 1849. We conclude therefore that the life time 1/470000 sec. is that of the transition from the 7.1 level to the 6.7 level. The radiation, if any, accompanying such a transition would be in the infra-red and would not affect the plate. The 1849 radiation resulting from the transition down from the 6.7 level accounts for the photoelectric current, but as the life of 1849 radiation is very short the life of the first transition is the one measured. The fact that this life time is independent of pressure makes it improbable that metastable atoms or radiation diffusion play any part in this persistence.

That this radiation is associated with the 7.1 break is in accord with the fact that it was most prominent for pressures corresponding to temperatures greater than 30°C. The critical potential curves show that the radiation associated with the 7.1 break is a much greater fraction of the total radiation at high temperatures than at low. (Cf Fig. 2, Curve *a* at 60 and Curve *b* at 10°C.)

Another radiation was observed having a value of $1/T$ roughly equal to 120000 (between 100000 and 200000). It was never isolated sufficiently for precise measurement, but usually was masked by 2537 and manifested itself only as an irregularity in the curve. (See Fig. 3, Curve *c*.) In several cases it stood out rather prominently owing to some condition which temporarily rendered the photoelectric surface quite insensitive to 2537. This condition was however transitory and no satisfactory curve for this radiation was obtained. To determine the break in the critical potential curve with which this radiation is associated, Curve *b* Fig. 5, similar to Curve *a*, was taken at 0°C with $G\text{-}F=5.4$ plus a variable alternating potential of 37500 cycles. At this temperature and for this frequency 2537 gives $R=100$ and the 120000 radiation gives $R=0.35$ (approximately). While the value of R for 6 volts peak

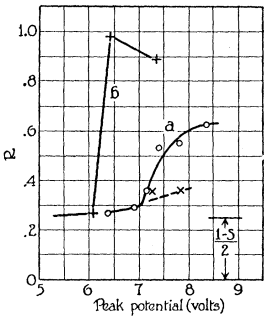

Fig. 5. *a*. Peak value of $G-F$ vs. R. Solid line, frequency 80,000; dotted line, frequency 500,000. *b*. Peak value of $G-F$ vs. R. Frequency 37,500.

value of G-F is lower than calculated, the error being probably due to the very small radiation at this voltage, the curve rises sharply to a value of nearly unity at 6.4 volts indicating that below 6 volts the 120000 radiation is a large part of the total but that above 6 volts 2537 becomes predominant. The curve drops to 0.95 at 7.4 volts due probably to the increase in the 470000 radiation.

These results indicate only that this 120000 radiation is excited below 6 volts. It seems probable that it is either one of the molecular bands excited between 5 and 6 volts or that what was measured was the life of a transition to the 4.86 volt level giving itself no radiation capable of affecting the nickel plate but followed by 2537.

PHYSICS LABORATORIES,
COLUMBIA UNIVERSITY,
November 20, 1928.