VOLTAGE-INTENSITY RELATIONS OF MERCURY LINES BELOW IONIZATION

By D. R. White

Abstract

Accelerating voltage-intensity relations have been obtained for twenty-eight lines of the mercury spectrum (between 5500A and 2500A) excited by electronic bombardment at potentials less than the ionization potential. The tube in which the radiation was excited had four electrodes, hot cathode and three grids, and the observations were made by photographic spectrophotometric measurements. In agreement with the results of other workers, the minimum potential of excitation of a line is found to agree closely with the theoretical value in all cases but one. The curves representing the voltage-intensity relation for lines with a common outer orbit are found identical when the intensity scales are so chosen as to arbitrarily make the curves coincide at one point. Upward and downward breaks are found in these curves at certain critical potentials but the character of the breaks and the potentials at which they occur change from series to series. The *ratio of the numbers of quanta emitted* in the lines of the triplet $2p_1-2s(5461)$, $2p_2-2s(4358)$, $2p_3-2s(4047)$ with an accelerating voltage of 10.2 volts was found to be 9 : 11 : 3.

Introduction

It HAS been shown by Eldridge,[1] Hertz,[2] Hughes and Hagenow,[3] and Newman,[4] that it is possible to excite in stages the arc spectrum of each of a number of elements. This group by group excitation is simply explained by the Bohr theory. Each group of lines is found to contain only lines having a common outer orbit and the number of lines, then, in any group depends upon the number of transitions corresponding to emission of radiation which begin at that orbit. Such transitions may take the valence electron to its normal orbit in one step or they may be the first of a series of transitions which carries the valence electron to its normal orbit. Each of these groups was found to be present only when the energy of the bombarding electrons was greater than the minimum necessary for a single impact to raise the valence electron from its normal orbit to the outer orbit which was common to the group of lines.

Hertz and de Visser[5] went farther than this and investigated in detail the relation between the voltage of excitation and the intensity of light

[1] J. A. Eldridge, Phys. Rev. **23,** 685 (1924).
[2] G. Hertz, Zeits. f. Physik **22,** 18 (1924).
[3] A. Ll. Hughes and C. F. Hagenow, Phys. Rev. **24,** 229 (1924).
[4] F. H. Newman, Phil. Mag. **50,** 165, 796 and 1276 (1925).
[5] G. Hertz and J. C. Scharp de Visser, Zeits. f. Physik **31,** 470 (1925).

emitted for a few of the lines of helium and neon. They studied two helium lines and four neon lines which lie in the visible region of the spectrum. In the case of mercury we have found it possible to push this type of investigation further by use of a tube which gave a greater intensity of light than appears to have been previously obtained. Voltage-intensity curves are presented here for twenty-eight lines of the mercury spectrum lying in the region 5500A to 2500A.

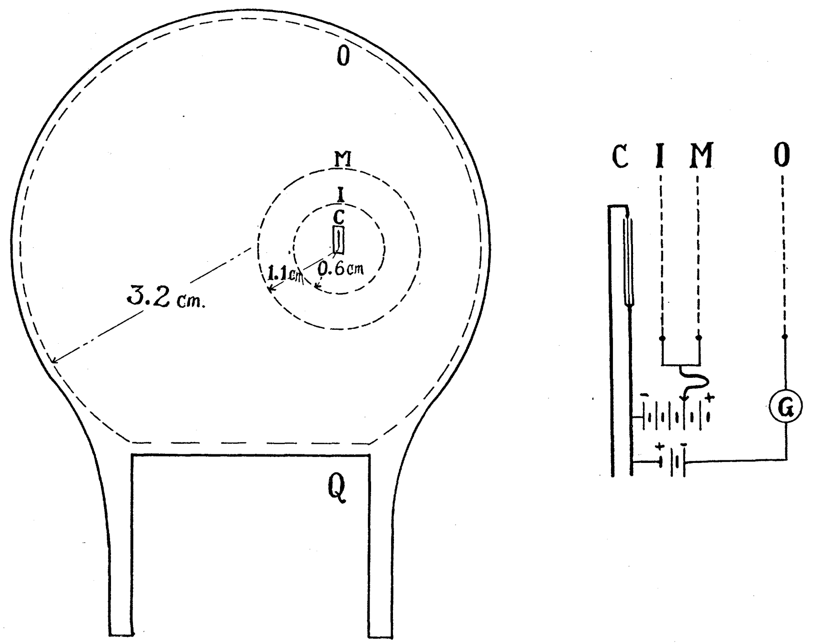

Fig. 1. Cross section of the experimental tube and the essential electrical circuits.

Apparatus and Experimental Details

A cylindrical tube, about 6.5 cm in diameter and 20 cm long was used for this investigation. A horizontal section of it is shown in Fig. 1 with the grid diameters indicated. The equipotential oxide coated platinum cathode[6] *C* was 4 mm wide by 37 mm long and was surrounded by two cylindrical grids *I* and *M* as shown. These grids were made of nickel gauze, 7 meshes per centimeter and wires 0.29 mm in diameter. They extended at both ends about 30 mm beyond the cathode and were supported on the glass arm that carried the leads to the cathode. A variable voltage was applied to these by means of the batteries indicated. The

[6] The cathode was similar to that described by Harold W. Webb, Phys. Rev. **24,** 116 (1924).

grid O, also of nickel gauze, lined the walls of the tube, and was kept at a potential of -3 volts with respect to the cathode for most of the experiments and had in its circuit a galvanometer G which measured the current to it. The reentrant quartz window Q permitted spectroscopic study of the radiation produced within the tube.

The gas was removed from the tube by continuously operated pumps connected near its top which kept the residual gas pressure less than 5×10^{-5} mm. At the same time the supply of mercury vapor was maintained by evaporation from a drop of mercury at the bottom of the tube

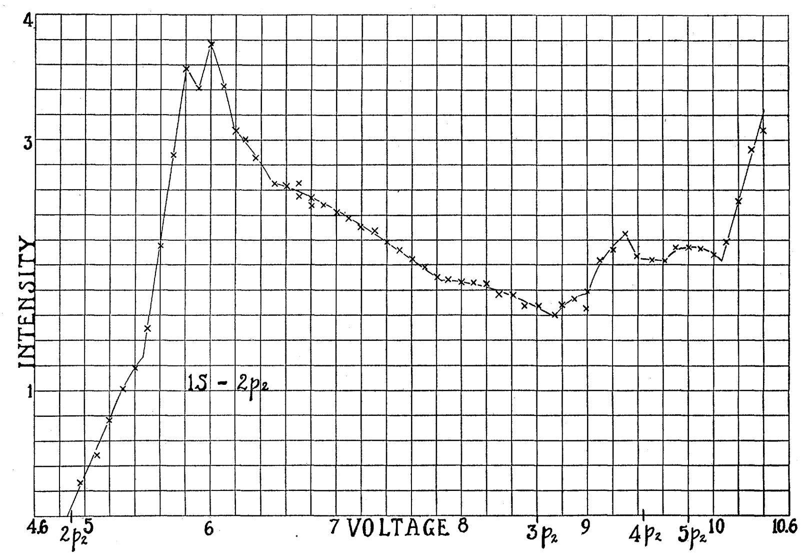

Fig. 2. Accelerating voltage-intensity relation for the line $1S-2p_2(2537)$.

which was heated by an electric heater. No accurate estimate of the mercury vapor pressure can be given for these conditions as evaporation was taking place at approximately 230°C and condensation at approximately 40°C. However an accurate estimate of the vapor pressure is of no particular importance as the results were not found to change materially for evaporation temperatures varying between 210°C and 250°C.

The spectroscopic observations were made with a small quartz spectrograph which gave a dispersion of 7A per millimeter in the region of 2500A. In the region of 3600A the dispersion was less so that, when the slit was opened sufficiently to give line widths great enough for satisfactory density measurements, the lines overlapped in each of the groups[7] $2p_1-mD$, $2p_1-md_{123}$; $2p_2-mD$, $2p_2-md_{23}$; and $2p_3-mD$, $2p-md_3$.

[7] Paschen-Gotze, Seriengesetze der Linienspektren, p. 116 (1922).

(For brevity these groups of lines will be designated as $2p_1 - mDd_{123}$, $2p_2 - mDd_{23}$ and $2p_3 - mDd_3$ respectively.)

The densities were measured by means of a densitometer in which the relative intensity of the light transmitted by a small portion of the plate was measured by a photo-electric cell kindly furnished us by Dr. H. E. Ives. The photo-electric current was measured by balancing its *Ir* drop in a resistance of 20 megohms by a direct reading potentiometer. Both were placed in the grid circuit of a radio vacuum tube in such a manner that at the point of balance the plate current was unchanged as the

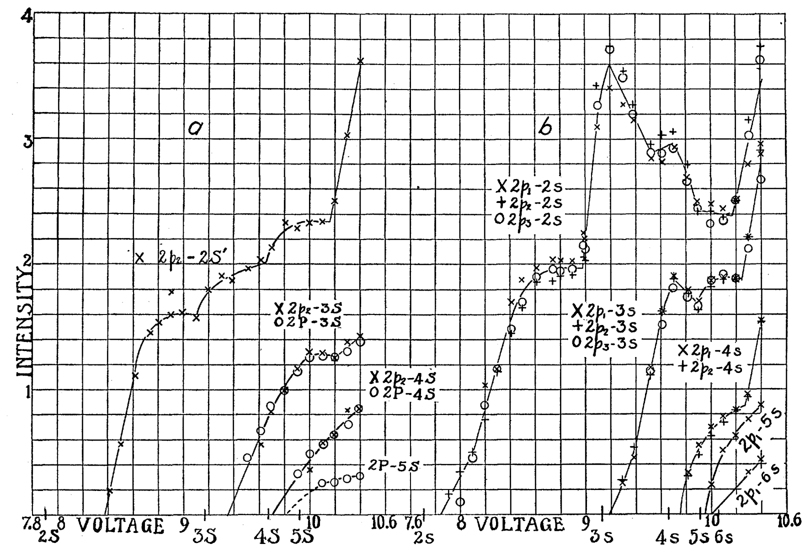

Fig. 3. Accelerating voltage-intensity relations for lines with *S* and *s* orbits as outer ones.

potentiometer and resistance were switched into and out of the grid circuit. A circuit, similar to that of a simple potentiometer, connected in the plate circuit of the vacuum tube made it possible for a galvanometer to detect smaller changes of current than could a meter capable of carrying the entire plate current. This arrangement was found necessary to attain the precision desired.

When the tube was operated, electrons came from the grounded cathode *C*, were accelerated in the space between *C* and *I* and then were allowed to move freely in the space between *I* and *M* which was kept free from externally applied fields by directly connecting *M* to *I*. Upon entering the space between *M* and *O* the electrons were slowed down and were then returned to either *M* or *I* by the negative potential on *O*. Under these conditions it was observed that the radiation was excited in a space represented by a hollow cylinder having the grid I for its inner surface and an outer diameter some 5 mm greater than the diameter of M. This volume, in which the radiation originated, remained approximately constant for voltages more than half a volt below the ionization potential but increased rapidly for higher voltages and entirely filled the tube at the ionization potential.

The theoretical value for the ionization potential is 10.4 volts but it was found to be an applied accelerating potential varying from week to week between the limits 11.6 and 12.0 volts. The difference, which was

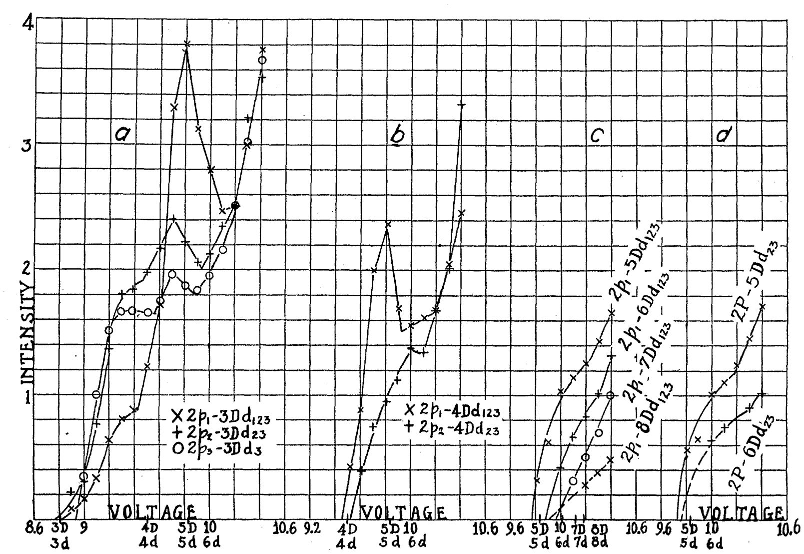

Fig. 4. Accelerating voltage-intensity relations for lines with D and d_{123} orbits as outer ones. Groups of lines for which the frequency difference is due to energy differences of the D and d_{123} orbits were not separated with the spectrograph used.

the voltage correction subtracted from all the accelerating voltage readings of any series, was due to a 0.2 volt drop in the leads and a variable correction due to contact difference of potential and the initial velocity of the electrons from the cathode. The ionization potential was determined by means of the galvanometer G in the circuit of the grid O. Since this grid was at a sufficiently great negative potential with respect to the cathode to keep electrons from reaching it, the current from it, through the galvanometer, must have been due to leakage across the insulation and to positive ions. An accelerating voltage-galvanometer current curve for the second of these components should show a very great increase of slope when the speed of the electrons is such that a single impact can just ionize an atom, while the first component should not show any such characteristic. The accelerating voltage corresponding to this abrupt increase of slope was taken as the ionization point.

Results

The results of the investigation are presented in the typical accelerating voltage-intensity curves Figs. 2, 3 and 4. The curves are grouped according to the outer orbit of the transition. Fig. 2 shows the curve for the transition $1S-2p_2$. Fig. 3 shows curves for transitions with ms and mS as outer orbits. Fig. 4 gives the curves for transitions $2p_i-mDd_{123}$. Table I lists the lines observed and gives an approximate idea of their relative strengths. The first column gives the notation for the transition, the second gives the wave-length, the third gives the symbol used to designate the points on the curve and the fourth gives the photographic density for an accelerating potential of 10.2 volts and hence an approximate idea of the relative strength of each line.

Table I

The lines observed and their photographic density at 10.2 *volts*

Notation	λ	Symbol	Density	Notation	λ	Symbol	Density
	Fig 2				Fig 4(a)		
$1S-2p_2$	2537	×	1.24	$2p_1-3Dd_{123}$	3650	×	1.70
	Fig 3(a)			$2p_2-3Dd_{23}$	3125	+	1.34
$2p_2-2S$	4078	×	.72	$2p_3-3Dd_3$	2967	○	.72
$2p_2-3S$	2858	×	.10		Fig 4(b)		
$2P-3S$	4916	○	.32	$2p_1-4Dd_{123}$	3025	×	.69
$2p_2-4S$	2563	×	.03	$2p_2-4Dd_{23}$	2652	+	.56
$2P-4S$	4108	○	.34	$2p_1-5Dd_{123}$	2803	×	.30
$2P-5S$	3801	○	.02	$2p_1-6Dd_{123}$	2698	+	.11
	Fig 3(b)			$2p_1-7Dd_{123}$	2639	○	.03
$2p_1-2s$	5461	×	.80	$2p_1-8Dd_{123}$	2603	×	.01
$2p_2-2s$	4358	+	1.48		Fig 4(d)		
$2p_3-2s$	4047	○	1.11	$2P-5Dd_{23}$	3906	×	.15
				$2P-5Dd_{23}$	3704	+	.03
$2p_1-3s$	3341	×	.52				
$2p_2-3s$	2893	+	.44				
$2p_3-3s$	2752	○	.18				
$2p_1-4s$	2925	×	.22				
$2p_2-4s$	2576	+	.18				
$2p_1-5s$	2759	×	.05				
$2p_1-6s$	2674	×	.01*				

*Density at 10.3 volts.

For all curves obtained in these experiments, spectrograms were made in order of increasing voltage at approximately 0.1 or 0.2 volt intervals. As more than one plate was needed in a series of spectrograms, exposures at two voltages were repeated on the second plate to insure continuity.

In addition, on each plate used, there was at least one group of three spectrograms for which the tube was held constant while the intensity was varied in known ratios by screens in the optical system of the spectrograph. The density-intensity relation thus obtained for any line was graphically extrapolated when necessary to obtain the complete voltage-intensity relationship for the line.

The corrected voltages are in all cases the abscissas of the curves. The correction used is known to only $\pm .05$ volt and hence all potentials are in doubt by that amount although the differences of potential between the points are known to $\pm .02$ volt. The ordinates are the intensities per milli-ampere emission and were obtained by dividing the intensity found from the photographic plates by the emission from the cathode when the spectrogram was taken. These ordinates have a precision of about 4 percent for most of the points though the accuracy is less at the lowest and the highest intensities of the lines.

A value of the minimum potential necessary for the excitation of the different lines was obtained by extrapolating the voltage-intensity curves to the voltage axis. The intercept thus found is the minimum value of the accelerating potential for excitation of the lines. This intercept agrees with the theoretical value, which is noted on the voltage axis of the curve, within the limit of accuracy of the extrapolation, in accordance with the conclusions of Eldridge and Hertz, for all lines but one. In the case of the transition $2p_2-2S$, $\lambda 4078$, the intercept is 8.3 volts while the theoretical value is 7.9 volts. It is possible that there is another break in the curve at an intensity below the limit of sensitivity of the method that would carry the curve to 7.9 volts.

In all cases where two or more lines had the same outer orbit, the curves representing the voltage-intensity relation were identical when the intensity scales were so chosen that the curves coincided at one point. This is shown in Fig. 3. Fig. 3(*b*) shows curves for the groups of lines $2p_i-2s$, $2p_i-3s$ and $2p_i-4s$ which have the common outer orbits $2s$, $3s$ and $4s$ respectively. The observed intensities, arbitrarily plotted as equal at 10.2 volts, are indicated by the symbols in the figure. Only one curve was drawn as that represents all points within the experimental error. In a similar manner the pairs of lines $2P-3S$, $2p_2-3S$; and $2P-4S$, $2p_2-4S$ are plotted in Fig. 3(a). The same close agreement between the curves is observed. This is of particular importance as each pair has one line belonging to the singlet series and one to the combination series.

The information obtained concerning the lines with D and d orbits as outer orbits is not sufficient to determine whether or not the same sort of similarity holds there also. This is due to the fact that the spectrograph did not separate completely groups of the type $2p-mDd_{123}$ since the multiplicity is due to the D and d_{123} levels which have small energy differences.

The result found in the cases of the ms and mS orbits leads to the conclusion that the ratio of the number of quanta corresponding to the transitions of the types $x-mz$, and $y-mz$ ($z=s$ or S) is independent of the voltage of excitation. This is equivalent to the statement that the voltage of excitation does not affect the relative probability that an electron in one of these outer orbits will take anyone of the possible paths from that orbit. This has been shown to hold for s and S orbits and may hold more generally.

The ratio of the number of quanta corresponding to each of the transitions $2p_1-2s$, $2p_2-2s$ and $2p_3-2s$, wave-lengths 5461, 4358 and 4047A respectively, was determined. Such a ratio of quanta is evidently also the ratio of the probabilities of the different transitions. Similar determinations were attempted for ratios of quanta for other groups of lines but, owing to experimental difficulties, were unsuccessful.

For the ratio measured, a vacuum type mazda lamp, operated at a color temperature 2420°K was used as the comparison source of known energy distribution for the spectrophotometric measurements since all three lines lie in the region of the spectrum but slightly absorbed by the glass of the lamp. The energy ratio for the lines 5461 and 4358 was determined by visual spectrophotometric comparison and a similar ratio for the lines 4358 and 4047 was measured photographically. After multiplying each energy ratio by the ratio of the wave-lengths to reduce to the ratio of the number of quanta, the latter was found to be

$$Q_{5461} : Q_{4358} : Q_{4047} = 255 : 300 : 82$$
$$= 9 : 11 : 3$$

within 5 percent the accuracy of the experiment. The measurements were made with an accelerating potential of 10.2 volts applied to the tube, but as already pointed out, this ratio was found to be independent of the voltage. Coblentz[8] finds for the ratio of energy of these lines in the arc the value 4 : 2 : 1.

The intensity variations of the lines as the accelerating potential passes through critical potentials is of considerable interest. The following discussion will be limited to potentials less than about 9.8 volts as the

[8] Coblentz, Long and Kahler, Bull. Bur. of Standards **15**, 1 (1919).

series terms are separated so little at higher voltages that the voltage change of 0.1 or 0.2 volt between spectrograms does not accurately show detail.

Fig. 3(b) shows that lines with an s orbit as the outer one have maxima at the minimum excitation potentials of succeeding s terms. That is, the probability of excitation of a term of the series shows a rapid increase starting 0.1 or 0.2 volt below the minimum excitation potential of a higher term of the series and marked decrease starting at that potential. Such character is very definitely shown by the curves for $2p_i-2s$ and $2p_i-3s$ in the region of the minimum excitation potentials of $3s$, $4s$ and $4s$ respectively.

In contrast with this behavior, Fig. 3(a) shows the curve representing the transition $2p_2-2S$ with upward breaks at the minimum excitation potentials of $3S$ and $4S$ terms. However, there are no breaks in the curves for $2P-3S$ and $2p_2-3S$ at the excitation potential of $4S$. The data indicate that such a break should have been found if present to an extent comparable with the breaks in the $2p_2-2S$ curve.

The curves in Fig. 4(a) representing transitions $2p_1-3Dd_{123}$, $2p_2-3Dd_{23}$ and $2p_3-3Dd_3$ show upward breaks at approximately the minimum excitation potentials of higher terms of the series. Only a very general resemblance can be expected in these curves since because of the small dispersion of the spectrograph they represent the result of superposing two or more lines, and the d orbits involved in the lines superposed are different for the different $2p$ orbits. The lines superposed, as indicated previously, are $2p_1-mD$, $2p_1-md_{123}$; $2p_2-mD$, $2p_2-md_{23}$; and $2p_3-mD$, $2p_3-md_3$.

The curves for the transitions $2p_1-4Dd_{123}$ and $2p_2-4Dd_{23}$ are shown in Fig. 4(b) and are markedly dissimilar. They show much less similarity than found in the case of the transitions previously mentioned, those from $3D$ and $3d_{123}$. Even the points of maxima and minima do not occur at the same voltages in the two curves.

The accelerating voltage-intensity relation for the resonance line $1S-2p_2$, (2537) was also determined. In the curve representing this relation, Fig. 2, there is an upward break between 5.4 and 5.5. volts which is believed to be due to the excitation of metastable atoms in the $2p_1$ state which pass over to atoms in the $2p_2$ state as a result of impacts of the second kind.[9] The downward break which is found at 5.8 volts corresponds most closely to the excitation of the molecular band theoretically occurring at 5.7 volts. The upward break coming at 5.9 volts

[9] Klein and Rosseland, Zeits. f. Physik **4**, 46 (1921).

need not be interpreted as evidence of any new form of excitation, but only that a saturation value has been reached for the excitation of the molecular band. This is suggested by the fact that the slope of the line joining the points at 5.9 and 6.0 volts is approximately the same as the slope below 5.8 volts. There is a very marked downward break at 6.0 volts. This is a potential at which Miss Messenger[10] has shown that there is a rapid increase in the production of metastable atoms and hence this break is believed to be due to some form of excitation which produces little radiation but many metastable atoms. The general downward trend of the curve which started at the 6.0 volt break continues as far as 8.7 volts but in this interval there are three rather weak upward breaks. The significance of the first two of these, at 6.2 volts and 6.5 volts, respectively, is not clear. It is worthy of note that Miss Messenger[10] found a point of increased formation of metastable atoms at 6.3 volts and it is possible that this is to be identified with one of these breaks just mentioned. The third of these upward breaks occurs at 7.8 volts and is believed to be due to the presence of transitions from $2s$ to $2p$ at potentials above this value. The upward break at 8.7 volts marks the end of the general downward trend and the beginning of an upward slope which continues to 9.3 volts where there is a downward break. The upward break at 10.0 volts marks the beginning of an upward slope which continues to the highest potentials used. The 8.7 volt break is probably due to returns to $2p_2$ from $3D$ and $3d_{23}$ although the theoretical minimum excitation potential for these orbits is 8.8 volts. Since the $3p_2$ orbit has an excitation potential of 8.6 volts, this upward break at 8.7 volts might be interpreted as indicating for the $1S-2p_2$ transition a behavior similar to that found for the $2p_2-2S$ transition which had an upward break at the minimum excitation potentials of upper terms of the series. Thus it is seen that it is possible that this 8.7 break is the result of more than one cause. At 9.0 volts there is an upward break in the curve which is believed to be due to the rapid increase in the excitation of $2s$ starting at this potential (See Fig. 3(b)) which thereby increases returns from $2s$ to $2p_2$ and hence increases emission of $1S-2p_2$. The interpretation of the breaks at the higher potentials is not possible as transitions from so many orbits above 9 volts lead to $2p_2$ that it is no longer possible to determine the cause of any given break.

In considering the characteristics of these curves no reference has been made to double impacts of atoms and electrons as such impacts were found to be relatively improbable. If double impacts had been present

[10] Miss H. A. Messenger, Phys. Rev. **28**, 962 (1926).

two effects would have been noted. First, there would have been an appreciable positive ion current to grid *O* at potentials below the ionization point. No such positive ion current was shown by the galvanometer *G* and there was no spectroscopic evidence of ionization. Second, if double impacts had been relatively probable, upward breaks at both 9.6 and 9.8 volts in the curve $1S-2p_2$ would be expected, the first due to excitation of $2p_1$ and $2p_2$ successively by an electron and the second due to successive $2p_2$ excitation. A small break at 9.6 is observed but none whatever at 9.8 volts. In view of these two tests, it is evident that double impacts produced no appreciable effect in these experiments.

In conclusion, I thank Professor Harold W. Webb, at whose suggestion the work was undertaken, for his continued interest and guidance in the work. I also thank Professor H. W. Farwell for his encouragement and the laboratory facilities which he placed at my disposal.

Phoenix Physical Laboratories,
Columbia University,
August 13, 1926.