THE SIGNIFICANCE OF CERTAIN CRITICAL POTENTIALS OF MERCURY IN TERMS OF METASTABLE ATOMS AND RADIATION

By Helen A. Messenger

Abstract

The critical potentials of mercury, as found by Franck and Einsporn using the modified Lenard method, were studied by a further extension of this method which separated the effects due to metastable atoms and those due to true radiation. Quartz and calcite filters were interposed between the excitation system (hot-cathode and grid) and the detecting system ("photo-electric" plate and grid) of a four-electrode tube containing mercury vapor. The critical potential curves ("photo-electric" current plotted against voltage on excitation system) taken with and without these filters interposed were compared, the difference in the currents giving a measure of the relative number of metastable atoms produced at each voltage. All the breaks found by Franck and Einsporn except those at 5.76, 6.73, and 8.35 volts were found to be associated with increased production of metastable atoms. The hitherto unexplained breaks found by them at 6.04, 6.30, 7.12, 7.46, and 8.09 volts were found to be due mainly to the formation of metastable atoms. The difference between the photo-electric currents with the quartz and calcite filters interposed gave a measure of the radiation lying between λ1650 and λ2200, that is of the molecular bands λ2140 and of λ1849. The latter radiation was found to be the cause not only of the 6.7 volt break but also of that at 8.35 volts. The break at 7.73 volts is interpreted as the combined effect of radiation due to excitation at 7.69 volts and at 7.83 volts. The use of "photo-electric" plates of metals with different photo-electric characteristics gave further checks on the above conclusions.

THE critical potentials of mercury have been studied in great detail both by spectroscopic methods and by the Lenard method in various forms. As adapted by Davis and Goucher[1] in determining the nature of the resonance potentials at 4.9 and 6.7 volts and the ionizing potential at 10.4 volts, the Lenard method employs an excitation system having a hot cathode as a source of electrons surrounded by an accelerating grid to give them the desired velocities and a detecting system consisting of photo-electric plate and grid. By this method Franck and Einsporn[2] located eighteen critical voltages of which thirteen correspond to recognized energy levels at which either radiation occurs or the atom is known to become metastable, and five remain unexplained. Webb, using voltages not exceeding 5.2 volts and a photo-electric plate of nickel, found that in this case practically all the "photo-electric" effect was due

[1] Davis, B. and Goucher, F. S., Phys. Rev. **10**, 101 (1917).

[2] Franck, J. and Einsporn, E., Zeits. f. Physik **2**, 18 (1920).

to the action of metastable atoms on the plate.[3] He found further that with a quartz filter between the excitation and detecting systems the plate current for all voltages was greatly diminished and that below 6.0 volts no photo-electric current could be detected. The present experiments were undertaken to determine in greater detail the part played by metastable atoms at the various critical potentials and that by the radiant energy resulting from the excitation of the atom.

The essential feature of the method here used is to obtain "photo-electric," or better "plate" current-voltage curves by the method outlined above with and without filters of quartz or calcite interposed between excitation and detecting systems. These filters transmit certain radiations but cut off atomic carriers of energy, i.e., metastable atoms. By subtracting the plate current obtained with the quartz filter interposed (after correcting for its light absorption characteristics) from the plate current obtained without a filter a measure of the number of metastable atoms formed was obtained.

By using filters with known transmission characteristics and plates of different materials, the method was extended to identify some of the radiations excited at the various critical voltages and to show the relative importance of the effects due to these radiations and to metastable atoms.

Apparatus and Experimental Procedure

Three four-electrode tubes designated as tubes I, II and III were used. In Fig. 1 the essential details of tubes II and III are given. The unipotential hot-cathode *F* was of the form described by Webb.[3] The glass tube supporting it was held in a ground glass joint and extended perpendicular to the plane of the diagram. The cylinder *G* is the accelerating grid surrounding the hot-cathode *F*. The "photo-electric" plate *P* was supported by an insulating quartz tube through which the lead wire passed to the electrometer connection at *E*. The slide *S* carrying three windows, one open, the other two covered respectively with quartz and calcite, moved easily in the nickel frame *D*, which, for rigidity, was of sheet metal with the exception of the side facing the cathode, where nickel mesh was used. An opening in this frame *D* opposite the plate *P* and in line with the hot-cathode *F* was covered by the "photo-electric" grid *H*. By turning the winch *W* in its ground glass joint the quartz or calcite filter could be lowered so as to cover this opening. As the semi-cylindrical nickel box *B* which surrounded the plate *P* was light-tight and welded to *D* the only entrance to the plate *P* for radiation or metastable atoms was through *H*.

[3] Webb, H. W., Phys. Rev. **24**, 113 (1924).

Tubes II and III were identical except that in tube II the plate was of nickel and in tube III of aluminum. With the exception of this aluminum plate and of the platinum cathode all metal parts in all three tubes were of nickel.

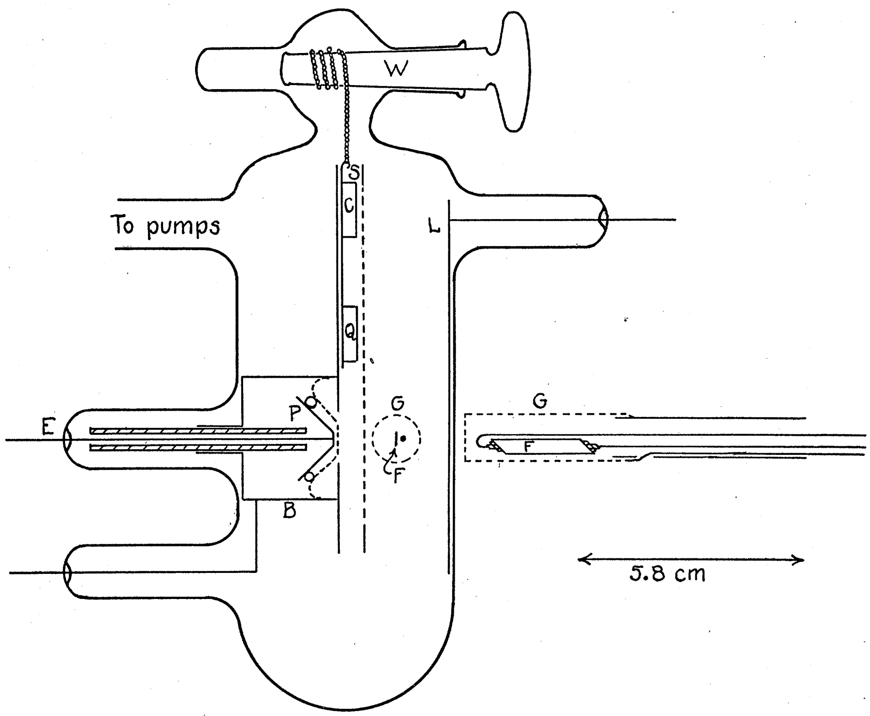

Fig. 1. Diagram of experimental tubes II and III.

The plate P was a disk folded along a diameter so that the halves formed an angle of about 90° (the fold being placed parallel to the cathode). The grid H was bent to the same general form and insulated from the plate by small quartz rods. This form of the detecting system was used to avoid possible effects due to the collecting of electrons on the face of the quartz toward the plate which would tend to inhibit further photo-electric action.

Tube I differed from the above in that it lacked the sliding windows and had a plate of different form. Filters of quartz and calcite were placed inside the tube when it was blown. A side tube of which the end could be opened made it possible to reach in with forceps and place in position either the quartz or calcite filter, after which the tube was resealed. The advantage of this arrangement was that larger windows and filters could be used which increased the plate current making it possible to locate the critical points on the curves with greater precision. This tube was used to study the details of the individual curves. The plate was a disk mounted with its surface parallel to the plane "photoelectric" grid at a distance of 3 mm. When in use the quartz window rested against this grid so as completely to cover the opening to the box containing the plate and to prevent the entrance of the metastable atoms.

In all these tubes a metal lining L which was kept at a known voltage prevented the collecting of charges on the glass wall which might result in spurious breaks in the curves,[4] and also served to shield the tube from outside disturbances. The tube was further shielded by metal foil wrapped closely about the outside and well grounded.

The temperature of the walls of the tube was held constant to within 0.5°C by a low speed fan which forced air heated by coils of wire in an adjoining oven into the asbestos lined box containing the experimental tube. The air flow was controlled by baffle plates adjusted until they kept the temperature uniform throughout the box.

The tube was pumped until the pressure of the residual gas was less than .0002 mm by means of a Langmuir condensation pump in series with a fore-pump. The pumps were kept running during readings.

Plate currents were measured by a Compton electrometer with a sensitivity of 2000 mm per volt. Accelerating voltages were measured by a Wolff potentiometer. The emission current was measured by a microammeter in the cathode-grid circuit The microammeter reading was taken simultaneously with each electrometer reading. The current E plotted on the curves in this paper is the electrometer current divided by the emission current.

Throughout the experimental work the negative end of the platinum strip which formed the heater of the cathode was in electrical contact with the surrounding equipotential sheath which was insulated from the heater at all other points The accelerating voltage was applied between this equipotential point and the grid G. The measured accelerating voltage was therefore the maximum voltage drop that could be obtained between the grid G and any part of the hot-cathode.

The voltage correction for drop in the leads and contact potential difference was obtained by locating the ionization point by the method of Davis and Goucher[1] and checked by the value of the lowest critical potential, 4.7 volts, which was always found as a well defined break in the resonance potential curves when no filter was interposed between

[4] Olson, A. R. and Young, T. F., Phys. Rev. **25**, 58 (1925).

the excitation and detecting systems. When the curves were corrected certain marked peculiarities of form which characterized the various curves were repeated at the same voltages and gave additional evidence of the accuracy of the correction. Throughout this paper the correction has been applied to all voltages cited and plotted on curves.

As the "photo-electric" sensitivity of the plate P varied with time, it was necessary, for a reliable comparison of the effects on the plate when no filter was used and when a quartz or calcite filter was interposed between the excitation and detecting systems, to obtain data for the resonance potential curves rapidly. With the sliding windows of tubes II and III it was possible to remove either filter and leave the window open or to close the window by interposing either filter in approximately one second. As a result the total time required to measure the plate current for all three windows at a given voltage was reduced to that required for the readings alone. To avoid the effect of changes in the plate on the form of the curve as a whole these sets of three readings were taken at .5 volt steps and the details interpolated from curves taken separately at consecutive .1 volt steps from 4.0 to 11.0 volts for each filter and for no filter but at the same temperature and with the same distributions of voltage.

The filters of quartz and calcite and the plate materials nickel and aluminum were chosen because they separated the effects of the various radiations emitted to the best advantage. The properties which led to their selection are summarized below to aid in the interpretation of the curves which follow. The wave-length ranges of the radiations in mercury vapor which can and can not be detected by the present apparatus are also specified.

Properties of filters and plates

Filter	Minimum wave-length transmitted	More than 60 percent transmitted	Important mercury lines and bands not transmitted
Quartz	1650A[5]	$\lambda > 1800$A[5]	1403, 1269A
Calcite	2200A[5]	$\lambda > 2400$A[5]	2140, 1849A 1403, 1269A

Plate	Photo-electric long wave-length limit	Photo-electric effect of λ2537
Nickel	2500A[6]	Not measurable
Aluminum	2700A[6]	Marked

Wave-length Ranges of the Radiation Detected by the Present Apparatus

Less than 1650A.—These wave-lengths affect the plate when no filter is used but their effect is not separable from that of metastable atoms. Owing to the large effect of the latter the effect of these short waves is considered negligible.

1650–2200A.—This wave-length range is transmitted by quartz but not by calcite. The response of the plate to it is given by the difference between the photo-electric currents when using quartz and when using calcite as filter.

[5] Pflüger, Phys. Zeits. 5, 215 (1904).

2200–2500A.—This range of wave-lengths is transmitted by calcite and produces a photo-electric current from the nickel plate.

2200–2700A.—This range of wave-lengths is transmitted by calcite and produces a photo-electric current from the aluminum plate.

2500–2700A.—This range of wave-lengths is transmitted by either filter and produces a photo-electric current from aluminum but not from nickel.

WAVE-LENGTH RANGE OF RADIATION WHICH PRESENT APPARATUS CANNOT DETECT

Greater than 2700A.—These which are not detected by either plate are in the visible and infra-red regions of the spectrum and form a large part of the total radiation.

The transmissibilities of the filters were tested before they were used and after they had been in the tube for several months. They were found to be unchanged provided they had not been exposed to the arc used to sensitize the hot-cathode.

The photo-electric threshold of nickel has been given by Nielsen[6] as approximately 2500A. As he worked with outgassed metal while the plates used in the present experiment were only cleaned and sand-papered this upper wave-length limit was verified for the nickel plate used, by focussing on the plate monochromatic light from a metal spark dispersed by a quartz spectrograph. The effect of 2500A was not measurable while that of 2300A was marked. Evidently the nickel plate used did not respond to $\lambda 2537$ to a measurable extent.

RESULTS AND DISCUSSION

The results of the measurements are given by curves in Figs. 2, 3, 4 and 5, and in Table I.

Fig. 2 shows three typical curves obtained with tube II (nickel plate). Curve (*a*) is that taken with no filter; curve (*b*) is that with the quartz filter in place; curve (*c*) with the calcite filter in place. Curve (*a*) shows all the critical points found by Franck and Einsporn. (See Table I, column 1.) The most notable feature of this set of curves is the large decrease in the plate current when either filter is interposed. The ratio of the plate current measured when using no filter to that when using a quartz filter is at times as high as 30:1 for voltages above 6 volts; its value is least between 5.3 and 6.0 volts; below 5.3, the lowest voltage at which radiation is detected, (see curves (*b*) and (*c*)) the value of this ratio approaches infinity.

It may be observed that although curve (*a*) (no filter) shows the same critical points as (*b*) (quartz filter) above 5.3 volts, the curves are not similar in form, as (*a*) builds up more rapidly at low than at high voltages and (*b*) builds up more rapidly at high than at low voltages. The calcite curve (*c*) shows no critical points at 5.7, 6.7, and 8.3 volts, and the break

[6] Nielsen, J. R., Phys. Rev. **25**, 30 (1925).

TABLE I

Critical potentials of mercury and some interpretations of their significance

Given by Franck and Einsporn.	Calculated from theory[9]	Interpreted from theory[9]	Found experimentally using— no filter	quartz filter	calcite filter	Plate	As interpreted from curves and data here given. Type of radiation indicate or implied	Number of metastable atoms.
1	2	3	4	5	6	7	8	9
4.68	4.66	$1S-2p_3$	4.70	....	....	Ni	None	Medium
			4.70	....	....	Al		
4.9	4.86	$1S-2p_2$	4.90	....	....	Ni		Small
			4.90	4.90	4.90	Al	2537, $1S-2p_2$	
5.3	5.28–	Molecular	5.25	5.25	5.25	Ni	λ<2500, >2200	Medium
	5.34	band				and	probably 2338	(mole-
		2338−2313				Al	−2313	cules)
5.47	5.43	$1S-2p_1$	5.45	5.40	5.40	“	2537, $1S-2p_1$	Large
5.76	5.73	Ionization						
	5.77	Molecular	5.75	5.75	....	“	λ<2200, >1650	
		band					probably 2140	None
		2140						
6.04	....		6.00	6.00	6.00	“	λ>2200, <2700	Large
6.30	....		6.30	6.30	6.30	“	λ>2200, <2700	Small
6.73	6.67	$1S-2P$	6.70	6.70	....	“	1849, $1S-2P$	None
7.12	....		7.10	7.10	7.05*	“	λ<2200, >1650	Medium
7.46	....		7.45	7.45	7.45*	“	λ<2200, >1650	Large
	7.69	$1S-2s$				“	4046, $2p_3-2s$	Medium
							4358, $2p_2-2s$	
							5461, $2p_1-2s$	
7.73			7.75			“	2537, $1S-2p_2$	
	(7.83)	($1S-2S$)		7.80	7.80*	“	4077, $2p_2-2S$	
							10139, $2P-2S$	
							1849, $1S-2P$	
8.09	....		8.00	8.05	....	“	λ<2200, >1650	Very small
8.35	....		8.30	8.30	....	“	λ<2200, >1650	
							probably 1849	None
8.64	8.58	$1S-3p_{2,3}$	8.60	8.60	8.60	“	13672, $2s-3p_2$	
							13950, $2s-3p_3$	Very small
							4046, $2p_3-2s$	
							5461, $2p_1-2s$	
8.86	8.79	$1S-3P$	8.80	8.85	8.80*	“	λ<2200, >1650	
	8.80–	$1S-3D$					5791, $2P-3D$	
	8.82	$1S-3d_{1,2,3}$					1849, $1S-2P$	
	8.80	$1S-3p_1$					3663, $2p_1-3D$	Small
							3131, $2p_2-3D$	
							2967, $2p_3-3D$	
....	9.15	$1S-3s$	9.15	9.15	9.20	“	3341, $2p_1-3S$	Very small
	9.19	$1S-3S$					2894, $2p_2-3S$	
							2735, $2p_3-3S$	
9.37	9.32	Successive	9.30	9.30	....	“	None	Large
		impacts						
		$1S-2p_3$						
9.60	9.52	Successive	9.50	9.55	....	“	2537, $1S-2p_2$	Medium
		impacts						
		$1S-2p_2$						
		$1S-2p_3$						
9.79	9.72	Successive	9.70	9.70	9.70	“	2537, $1S-2p_2$	Small
		impacts						
		$1S-2p_2$						
10.38	10.39	Ionization	10.4	10.4	10.4	“	All types	Medium

* Weak break.

Precision of observed critical points ± .05 volt.

at 8.1 volts is missing or very weak. In general the breaks above 8.0 volts on all curves taken with the calcite filter in place are difficult to locate precisely as none of them are well defined.

Measurements were made at 28°C, 55°C and 89°C. Those given in the form of curves in Fig. 2, taken at 89°C, are typical of all those obtained.

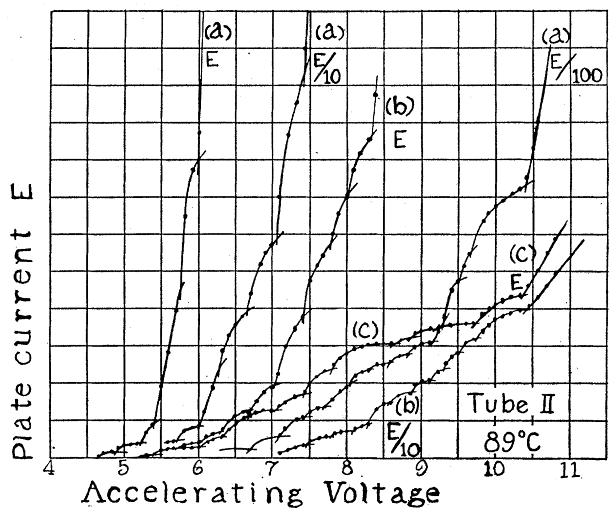

Fig. 2. Curves obtained with tube II (nickel plate), (*a*) using no filter, given in three parts with the electrometer current for two parts reduced by 10 and 100 for convenience in plotting, (*b*) using the quartz filter, given in two parts, (*c*) using the calcite filter.

At the higher temperatures the plate currents were larger at all voltages on all three curves; the ratio of the plate current with no filter to that due to radiation transmitted by quartz showed no significant change.

Fig. 3 shows how the metastable atoms increase with accelerating voltage. The ordinates are the differences between plate currents obtained at the stated voltages with and without the quartz filter between the excitation and detecting systems. They are therefore the differences between the plate current due to all forms of energy reaching the plate and that due to energy which reaches it as radiation. This curve is in three parts, the ordinates being reduced as indicated. The fact that this curve rises markedly at 4.7, 5.4, 7.8 and 8.8 volts indicates a marked increase in metastable atoms as a result of excitation at each of these voltages. It is known that metastable atoms are formed at levels corresponding to the two lower voltages, 4.7 and 5.4 volts (see Table I, column 3). Corresponding to the two higher voltages, 7.8 and 8.8, theory predicts that there are energy levels from which the valence electron may drop to either one of these metastable $2p$ orbits by emitting radiations which give rise to known spectrum lines (see Table I, columns 8

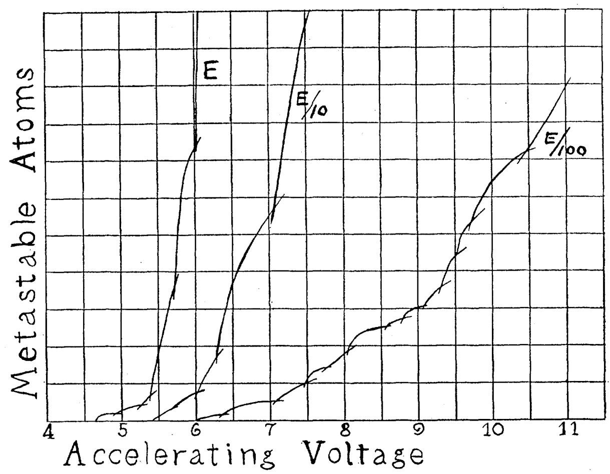

Fig. 3. Increase of metastable atoms with voltage. The ordinates are the differences between those of curve (a) and curve (b) in Fig. 2 at the voltages indicated.

and 9). The heretofore unexplained breaks of Franck and Einsporn at 6.0, 6.3, 7.1, 7.45 and 8.1 volts also occur on this curve. (The break at 8.1 volts is not listed by Franck and Einsporn but appears on their published curves.[2]) This indicates either that there are metastable levels corresponding to these critical voltages or else that the excitation at these voltages results in electron transitions to metastable orbits with or without radiation.

Fig. 4 shows the difference between photo-electric currents when quartz and calcite filters were used, plotted against accelerating voltage. This curve rises sharply at 6.7, 7.45 and 8.3 volts and to a lesser degree at 7.8 and 8.8 volts indicating that at these voltages there is an increase of radiation of wave-length less than 2200A but greater than 1650A since this is the range of the wave-length transmitted by quartz but not by calcite. The fact that this curve begins at 5.75 volts is of especial interest. The radiation from 5.75 to 6.7 volts is probably that of wave-length 2140A due to the molecular band at 5.73 volts observed by Wood and Guthrie,[7] as is suggested by Mohler.[8] At and above 6.7 volts the radiation represented by this curve is probably mainly λ1849.

[7] Wood, R. W. and Guthrie, D. V., Astrophys. J. **29**, 211 (1909).

[8] Mohler, F. L., National Research Council Bulletin, No. 48, Part II, pp. 70–71 (1924).

Fig. 5 shows three curves obtained (*a*) with no filter, (*b*) using the quartz filter, and (*c*) using the calcite filter with tube III (aluminum plate). Any differences between these curves and those of Fig. 2 must be due solely to the differences in the properties of the plates. Above 7.5 volts the two sets are similar in form; consequently only the parts of the curves for lower voltages are reproduced here. In curve (*a*) where no filter was used the lowest critical point is at 4.70 volts; in curves (*b*) and (*c*) the pure radiation curves, at 4.90 volts. This confirms the conclusion that the plate current from 4.70 to 4.90 volts is due solely to

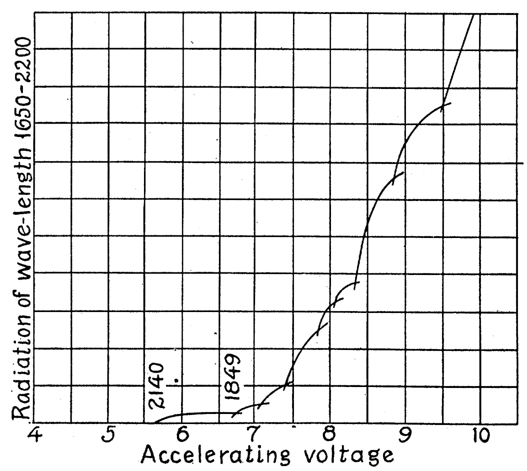

Fig. 4. Radiation of wave-length between 1650 and 2200. The ordinates are the differences between those of curves (*b*) and (*c*) in Fig. 2.

metastable atoms and is not a true photo-electric current. The radiation which is responsible for the initial rise in (*b*) and (*c*) is λ2537, which affects the aluminum plate. It may be observed that the ratio of the total plate current represented by (*a*) to the current due to pure radiation represented by curve (*b*) is smaller for the curves in Fig. 5 than for those in Fig. 2 due to the increase in the photo-electric current at all voltages resulting from the action of λ2537.

The breaks at 4.9 and 9.7 volts were attributed in the curves of Franck and Einsporn to λ2537, two successive impacts taking place at the higher voltage. The fact that the photo-electric response of the nickel plate used in the present experiment to that radiation is so small compared with its response to energy carried by metastable atoms makes it unlikely that this is the explanation of the breaks at these voltages in Fig. 2. They are probably due to a small number of metastable atoms produced as the valence electron drops from the 4.9 to the 4.7 orbit as the result of an atomic impact.

As stated earlier in this paper the value of the emission current was read simultaneously with each value of the plate current. When readings were taken with increasing accelerating voltage the emission current also increased and, plotted against this voltage, gave a curve in which there were upward breaks coinciding in many cases with the critical potentials. When the voltage was varied in the reverse direction the tendency of the emission curve to drop at these potentials was less marked. It was found that dividing the electrometer current by the emission current in no case removed from the resonance potential curves

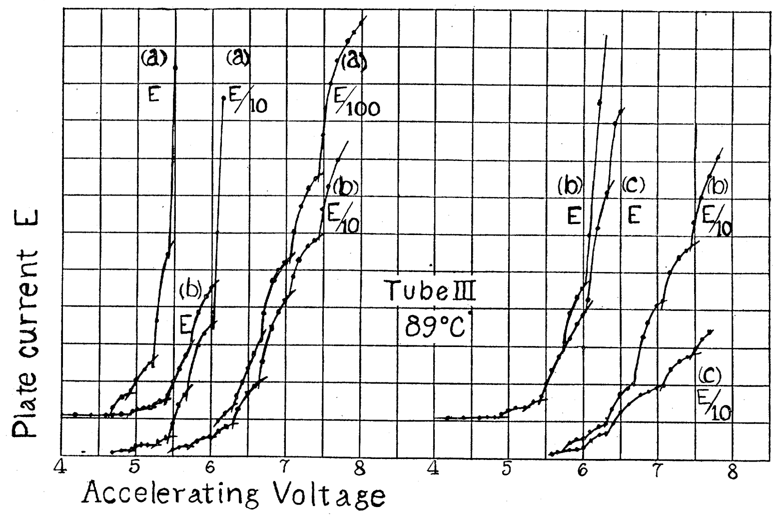

Fig. 5. Curves obtained with tube III (aluminum plate), (*a*) using no filter given in three parts the electrometer current for two being reduced by 10 and 100 for convenience in plotting, (*b*) using the quartz and (*c*) using the calcite filter, each given in two parts. Curve (*b*) is given twice, on the left with (*a*), on the right with (*c*) for clearness.

the breaks at the critical points recorded in the results (see Table I), whereas other intermediate spurious breaks observed on curves in which the electrometer reading was plotted directly, were eliminated.

Table I gives a summary of the experimental results. Column 1 gives for comparison the critical potentials found by Franck and Einsporn[2]; column 2 the corresponding values as calculated from theoretical considerations; column 3 gives the interpretation from the Bohr theory of the Franck and Einsporn critical points as given by Mohler[8]; columns 4, 5 and 6 give the critical points obtained in the present work with the filters listed at the heads of the columns; the plates used are specified in column 7.

Columns 8 and 9 give the author's interpretations of the experimental results, column 8 giving a description of the types of radiation indicated and column 9 indicating the relative number of metastable atoms produced at the various critical voltages. The manner in which these interpretations were reached has been discussed in the cases of some of the critical points, e.g., 4.7, 4.9, 5.4, 5.75 volts, etc.; the interpretations for other points are self-evident, e.g., those for 9.3, 5.25 and 6.7 volts; a few more need explanation.

It has been shown in connection with Fig. 3 that as a result of the excitation at the heretofore unexplained critical voltages 6.00, 6.30, 7.10, 7.45 and 8.10 volts metastable atoms are formed. The excitation at certain of these voltages also results in radiation of which the wave-length has been identified in some cases. At 6.00 and 6.30 volts, however, the evidence is not conclusive. At these voltages on both radiation curves obtained with the nickel plate the breaks are of similar magnitude. This indicates radiation of wave-length between 2200 and 2500A. On both curves with the aluminum plate these breaks are again similar to each other in magnitude but of greater magnitude than with the nickel plate. This indicates radiation of wave-length between 2200 and 2700A, which may be greater or less than 2500A. The increased magnitude of the 6.00 and 6.30 volt breaks with the aluminum plate may therefore be due either to $\lambda 2537$ or to the band $\lambda 2338$–13, the shorter wave-length radiation being more effective on the aluminum plate than on the nickel plate since it is farther from the upper photo-electric limit.

At 7.05, 7.45 and 8.05 volts, the fact that the breaks are weak or missing on the calcite curves, indicates the presence at these levels of radiation of wave-length <2200A and >1650A—probably $\lambda 2140$ or $\lambda 1849$.

The interpretation of breaks at higher levels is complicated by the fact that these levels are increasingly close and the radiation increasingly complex. It is not possible to do more from the present data than indicate a few facts that seem evident.

The break at 7.75 volts on the no-filter curves obtained with either nickel or aluminum plate is of interest as showing the possibilities of this method. The computed value corresponding to the $2s$ level is 7.69 volts; that corresponding to the $2S$ level is 7.83 volts. Mohler notes that the electron transition to the $2S$ level is not indicated in the Franck and Einsporn curves.[8] (It is given in brackets for that reason in columns 2 and 3 in Table I.) On the radiation curves in the present experiment the break always came at a higher voltage (7.83 volts) than on the curves taken with no filter (7.75 volts). It is evident that the 7.75 volt break is an average of the 7.69 volt break, due mainly to metastable atoms (see Fig. 3) and the 7.83 volt break due mainly to radiation. The observed effect of radiation is small at 7.69 volts because the electron transitions from the $2s$ to the metastable $2p$ orbits and to the $2p_2$ orbits give rise to visible radiations which cannot affect the plates and the effect of $1S-2p_2$ is weak in comparison with the effect of metastable atoms; it is larger at 7.83 volts since from the $2S$ level the transition $2P-2S$ may be followed by $1S-2P$, λ1849. That this is the correct explanation of this break is proven by the rise in the curve of Fig. 4 and the weak break in the calcite curve at 7.80 volts.

In all curves from measurements made with all three tubes when using the quartz filter, a well-defined break occurs at 8.30 volts, marking the excitation of a radiation that affects the slope of the entire curve above that point. There is no corresponding break on the calcite curve, so that beyond this voltage the two radiation curves are markedly unlike in form. This means that at 8.30 volts there is a large increase of a radiation of wave-length >1650A and <2200A which probably is λ1849, $1S-2P$. The next lower level corresponding to a known voltage is the $2S$ level corresponding to 7.83 volts. The known radiation λ10139 excited at 7.83 volts accompanies the electron transition $2P-2S$. If the excitation at 8.30 volts results in an infrared radiation as the valence electron moves to the $2S$ orbit it may be followed by the radiation $2P-2S$, λ10139, and then by $1S-2P$, λ1849. The two infrared radiations are beyond the wave-lengths detected by this apparatus but there is evidence of the existence of λ1849. Further evidence in favor of this interpretation of the 8.30 break is given by Eldridge[9] who reported that at 8.4 volts $2P-2S$, λ10139 was the strongest line in the observed spectrum although it did not appear on his published plates, as it fell in the infrared.

The break at 8.65 volts indicates electron transitions from the $3p_{2,3}$ levels accompanied by radiation of wave-length not detectable with this apparatus which finally leaves the valence electron in a metastable orbit. Since the infrared radiations λ13672 and λ13950, $2s-3p_2$ and $2s-3p_3$ are recognized radiations, it is probable that these occur and are followed by $2p_3-2s$ and $2p_1-2s$, in the visible region. This would account adequately for the small number of metastable atoms observed at 8.65 volts.

The question as to whether the large current attributed to metastable atoms might not be due in part to ionized atoms, was carefully in-

[9] Eldridge, J. R., Phys. Rev. **23**, 685 (1924).

vestigated by the method of Davis and Goucher.[1] Making the photo-electric grid negative with respect to the plate but keeping all other voltage distributions unchanged radiations and metastable atoms will produce a negative "photo-electric" current, while ionized atoms will tend to charge the plate positively and therefore decrease the negative current. With the grid positive with respect to the plate, radiation, metastable atoms and ionized atoms will produce a positive current. Consequently, if in comparing the plate currents obtained with these two arrangements of voltage the ratio of the positive to the negative is constant for all voltages, either the number of ionized atoms being formed is always proportional to the plate current (which is not probable) or the number formed is negligible. An increase with voltage in the ratio of the positive to the negative current would indicate the formation of ionized atoms at those voltages at which the ratio increased. No evidence of ionization was found below 10.4 volts. Furthermore a very careful study of that part of the curve between 5.0 and 6.0 volts showed that ionization was not the cause of the 5.7 volt break on the curves obtained with this apparatus.

It is of interest to compare the results of Franck and Einsporn with those given here. Evidently the effect of radiation was relatively greater in their apparatus, that of metastable atoms less. In the present apparatus the effect of radiation was the smaller of the two. The reason for these differences in sensitivity of the apparatus is not clear. With the exception of 4.70 volts, the voltages at which they report strong breaks are those at which the present work indicates the production of radiation. The breaks which are marked in the metastable atom curve of Fig. 3 are all listed among their weak breaks. The exception is the break at 8.35 volts which they list as a weak break although its interpretation in this work indicates that it is due to radiation.

The writer takes pleasure in acknowledging her indebtedness to Professor Harold W. Webb who suggested both the problem and the general method of attacking it and who has contributed much valuable criticism throughout the course of the work.

PHOENIX PHYSICAL LABORATORY,
COLUMBIA UNIVERSITY.
June 26, 1926.