IONIZATION EFFICIENCY OF ULTRA-VIOLET LIGHT IN CAESIUM VAPOR

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Abstract

Efficiency of photo-ionization in caesium vapor at 166°C as a function of wavelength.—Light from a quartz mercury arc after being resolved by a quartz spectrograph was passed through a tube containing caesium vapor. The energy of the radiation was measured with a Coblentz thermopile. The photo-ionization of the vapor was determined by drawing out the positive ions to a plate and measuring their number with an electrometer. The vapor pressure of the caesium was obtained by interpolation between existing data. The pressure at 166°C was taken as 0.027 mm which corresponded to an atomic concentration of 5.96×10^{14} atoms per cc. The efficiency of ionization B (the Einstein probability of absorption coefficient) was found to increase from 0.17×10^{-10} ions per atom per erg at 3345A to 3.4×10^{-10} at 3135A. The theoretical threshold is at 3184A. For shorter wave-lengths B diminished to a minimum of 1.2×10^{-10} at 2800A and then increased slowly for still shorter wave-lengths. The estimated possible error in B is 5 percent in relative values and 25 percent in absolute values.

Photoelectric efficiency from a caesium-gold alloy surface.—It was incidentally observed that caesium alloyed readily with a gold electrode and that the resulting surface was very active photo-electrically. The photo-sensitivity varied from 0.5×10^8 electrons per erg at 6100A to 2.0×10^8 at 2800A.

Introduction

IN THE last five years a very determined effort has been made to measure quantitatively the photo-ionization in alkali vapors as a function of the wave-length of the radiation. Kunz and Williams[1] were the first to detect electrically the ionization of a vapor by ultra-violet light. They found that radiation of wave-length greater than 3180A did not ionize caesium vapor at 140°–200°C but that wave-lengths shorter ionized it readily. It may be recalled that 3184A is the convergence wave-length of the caesium arc spectrum. Williamson[2] found for potassium vapor a critical wave-length of 2800–3100A in good agreement with the theoretical limit 2856A. He used graded filters to analyse the light, and to avoid surface effects, passed the light through a jet of the vapor. Lawrence[3] using the same form of tube but with a Pfund iron arc and monochromatic illuminator as a source, found 2610A as the limit and claimed that Williamson's data when corrected gave a similar value. He accounted for the discrepancy of 246A between his value and the theoretical one by supposing that in the jet many of the atoms were grouped into diatomic molecules which required 0.4 volts, corresponding to 246A, to separate them into atoms. Harrison and Slater[4] show that with

[1] Kunz and Williams, Phys. Rev. **15**, 550 (1920); **22**, 456 (1923).

[2] Williamson, Phys. Rev. **21**, 107 (1923).

[3] Lawrence, Phil. Mag. **50**, 345 (1925).

[4] Harrison and Slater, Phys. Rev. **26**, 176 (1925).

rapidly distilling sodium vapor at about 800°C there are about fifty times as many diatomic molecules as atoms.

More recently Mohler, Foote and Chenault[5] have applied to the problem the very sensitive method of detecting positive ions which had been developed by Kingdon[6] and Hertz[7] independently. By this method they were able to show that in caesium vapor the ionization efficiency in ultra-violet light is a maximum at about 3184A, the theoretical threshold, and that it decreases for shorter wave-lengths to about one-eighth of the maximum value at 2700A. They also found ionization at the resonance potentials corresponding to wave-lengths longer than 3184A, although close to 3184A the resolution was insufficient for separation of the peaks. We doubt whether ionization of such amount would take place in the normal vapor at the resonance wave-lengths without the heavy stream of electrons passing through. Mohler, Foote and Chenault's explanation of this ionization is that the light raises an electron to an outer orbit and a collision due to thermal agitation will lift it the rest of the way. The electrons in their tube had a velocity of about one volt—sufficient to ionize from the 4370A level. This velocity is 300 times the thermal velocity of the atoms, so most of the ionization was probably completed by electronic rather than by atomic impact. In Lawrence's work referred to above no such ionization at the resonance wave-lengths was found.

The photo-ionization of vapors by radiation of wave-length shorter than the arc spectrum limit is correlated with the absorption by the vapor of such radiation. Recently Harrison[8] by photographic and densitometer methods has quantitatively measured the absorption of light in Na vapor. His results on the variation of absorption with wave-length beyond the series limit closely resemble in general trend those of Mohler, Foote and Chenault on the variation with wave-length of photo-ionization.

The method used by Mohler, Foote and Chenault though very sensitive, did not lend itself to a quantitative determination of the photo-ionization as a function of the energy of the radiation. Moreover the presence of the slowly moving electrons was likely to confuse the measurements in the vicinity of the threshold wave-length because of their ability to complete the ionization by impact. The purpose of the present investigation is (1) a redetermination of the threshold wave-length, and (2) a determination of the absolute values of the ionization efficiency for various wave-lengths beyond the threshold.

METHOD

The general arrangement of the apparatus is shown in Fig. 1, A. A 110 volt D. C. Cooper-Hewitt mercury arc is the source. The current when it

[5] Foote and Mohler, Phys. Rev. **26**, 195 (1925); Mohler, Foote and Chenault, Phys. Rev. **27**, 37 (1926).

[6] Kingdon, Phys. Rev. **21**, 408 (1923).

[7] Hertz, Phys. Zeits. **18**, 307 (1923).

[8] Harrison, Phys. Rev. **24**, 466 (1924).

became steady after about thirty minutes, was 4.50 ± 0.05 amperes and the potential drop across the arc was about 50 volts. The current rose about 4 percent if the asbestos in front was removed, thus cooling the arc. The Hilger quartz spectrograph was fitted at the farther end with a slit a trifle larger, both vertically and horizontally, than the image of the first slit which was kept 10.1 by 0.75 mm in size. A system of screens, tubes, a lens and a sliding screen controlled by a string hung over glass rods, led the light to the furnace.

What was desired in illumination was a uniform cylinder of light, but as this was impossible (a point source would mean too little energy) the convergence of light to two images, one at each end of the tube, was deemed best. The objects for these two images were approximately 50 cm apart.
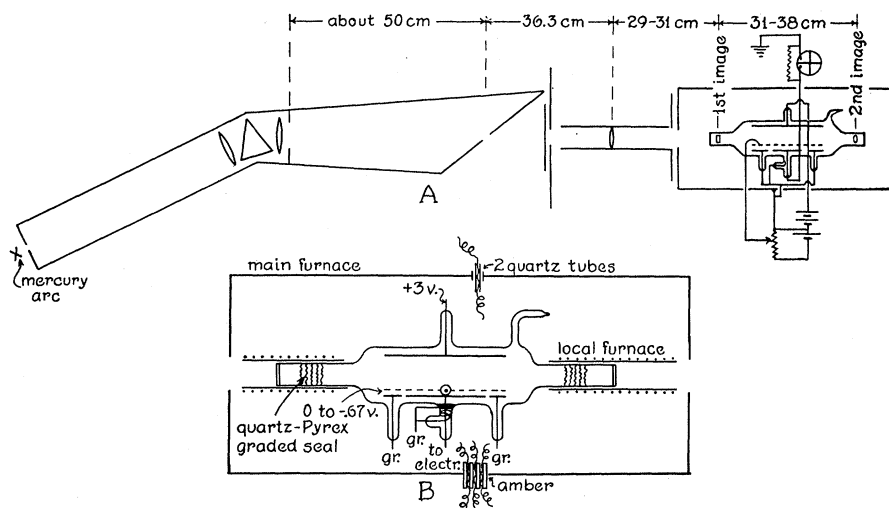

Fig. 1. A, arrangement of apparatus; B, detail of ionization tube.

One was an elliptical diaphragm (major axis 4.3 cm) just behind the second spectrograph lens, and the other was the image (1.3 cm high) of the first spectrograph slit. The light could not stray beyond the envelope of lines connecting the peripheries of the two images (except for aberrations). The shape and dimensions of the beam opposite the ends and at two intermediate points of the collecting plate were measured to determine the average cross section illuminated. This was done for two wave-lengths and a straight line graph was drawn to determine it at other wave-lengths. The average cross-section multiplied by the effective length of the collecting plate gave the volume from which the positive ions were collected.

The furnace was non-inductively wound. It had holes about 3.5 cm in diameter at each end, together with openings for a thermometer, and the electrical connections. The furnace, its accompanying lens, etc., were capable of being moved bodily with respect to the spectrograph.

The tube was made of quartz and Pyrex glass and is shown in Fig. 1. B. The plane parallel quartz plates attached to quartz-Pyrex seals were furnished by the Cooper-Hewitt Company. The grid consisted of 0.105 mm platinum wire with a spacing of 0.51 mm. Thus the fractional area between the wires was 0.628. The quantity of electricity collected on the plate was divided by this fraction to correct for loss to the grid. The mesh was pressed against a framework of stiff platinum wire in a hot flame at almost the melting point to fasten it firmly. The other electrodes were similarly made but with platinum foil substituted for the mesh. The framework was arc welded to a platinum hub into which the substantial tungsten leads were screwed. The length over all was 36.5 cm and the diameter of the main part was 6.2 cm. The quartz plates were 1.8 mm thick. To intercept surface currents, a grounded platinum spiral touched the glass all around the inside of the glass bell of the collecting electrode. Lead foil was wrapped around outside and grounded for the same reason. The guard electrodes at the ends of the collecting plate collected ions produced in the ends of the tube not opposite the collecting plate and made the region of production of the ions collected on the plate definitely calculable. The positive ions, rather than the electrons, were collected because thermal electrons from the walls and electrodes were always present. The grid was for the purpose of making the net current to the collecting plate zero in total darkness. If it were absent thermal electrons would usually make a troublesome current although in the second of the two runs, to give best results, the grid was kept grounded. The opposite plate was kept at three volts (less than ionizing potential) to drive positive ions to the collecting plate. Potentials as high as 10.5 volts, however, when tried after the last run, failed to produce any noticeable ionization by collision.

The electrometer had a sensitivity of 1500 mm per volt at 1 meter. A scale distance of 2.83 meters was used. A pencil resistance on hard rubber was used as a shunt. When best adjusted for our experiment its resistance was 1.173×10^9 ohms.

The spectrum was calibrated with a Coblentz thermopile of 26 hot junctions totalling 20 by 2 mm in area. The thermopile resistance was 11.2 ohms. The galvanometer had a resistance of 12 ohms and a figure of merit of 1.71×10^{-9} amp./mm at 1 meter. A scale distance of 3.33 meters was used. The thermopile was calibrated by placing it one meter from a Hefner lamp in a light-tight box. According to Coblentz[9] an unshielded Hefner lamp gives out 26 microcalories (± 6 percent) per sq. cm. per sec. at a distance of 1 meter. The slit of the thermopile was cut down to 1.45×0.18 cm (0.261 sq. cm) so as to make sure that all the light entering it reached the junctions. The energy entering the slit for 1 mm deflection of the galvanometer was found to be 0.637 ergs/sec.

Another thermopile tested was a stellar vacuum thermocouple of 1 pair of junctions made by Pettit and Nicholson[10] of the Mount Wilson Observa-

[9] Coblentz, Bull. Bur. Standards 11, 95 (1914).

[10] Pettit and Nicholson, Astrophys. J. 56, 295 (1922).

tory. On account of the difficulty of obtaining a sharply defined image of the slit on a target 1 mm square, it was no more sensitve than the Coblentz thermopile and was less reliable for this kind of work. Still another instrument experimented with was a coil thermopile studied by Wilson and Epps[11] and suggested to us by Dr. J. P. Cooley. It is a high resistance thermopile (700 ohms) with 100 pairs of junctions in a space of 1.5 cm. Thus it can be used with a galvanometer of high resistance and consequent high sensitivity. Although it gave twice the sensitivity of the Coblentz thermopile when used at atmospheric pressure, and six times when in an evacuated chamber with a quartz window, it was quite sluggish and required four minutes to reach half its final deflection. For this reason the Coblentz thermopile was finally used. It was sensitive enough and responded almost instantly.

Vapor pressure of caesium. There have been several determinations of the vapor pressure of caesium but unfortunately these were not made near
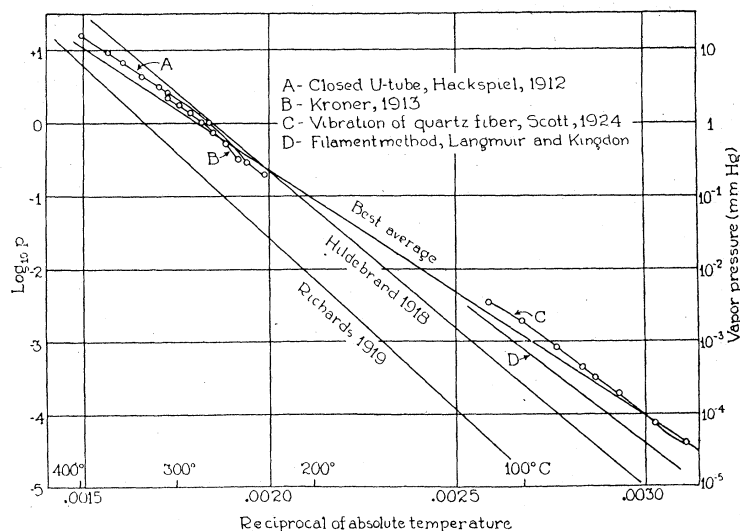

Fig. 2. Vapor pressure of caesium as a function of temperature.

166° and 204°C, the temperatures at which we worked. They have been made at 230°C and up by Hackspiel,[12] who used a closed U-tube method, and also at 120°C and down by Langmuir and Kingdon,[13] who measured the number of atoms striking an incandescent tungsten filament over 1100°C (all atoms then leave the filament as positive ions). Other determinations were made by Kroner[14] and by Scott[15] who used a vibrating quartz fibre method. These determinations are all shown in Fig. 2 where log p is plotted against the reciprocal of the absolute temperature of the vapor.

[11] Wilson and Epps, Proc. Phys. Soc. London **32**, 326 (1920).
[12] Hackspiel, Comptes rendus **154**, 877 (1912).
[13] Langmuir and Kingdon, Proc. Roy. Soc. **107A**, 61 (1925).
[14] Kroner, Ann. d. Physik **40**, 448 (1913).
[15] Scott, Phil. Mag. **47**, 49 (1924).

If we assume, with Hildebrand,[16] and others that such a plot should give a straight line, we obtain the most probable value of the vapor pressure by drawing the straight line which best fits the four sets of experimental data. For a temperature of 166°C we thus find that $p = 0.027$ mm Hg and at 203.9°C it is 0.107 mm Hg. The corresponding numbers of atoms per cc are 5.96 and 21.70×10^{14}.

RESULTS

(a) *Energy distribution in the mercury spectrum.* In measuring the photo-ionization of the caesium vapor the light was passed straight through the tube so that account must be taken of both transmission losses at the first quartz window and of the gain by reflection at the second window. In some incidental measurements of the photoelectric effect from a caesium-gold alloy surface the light was passed obliquely through the tube. In this case only transmission losses at the first plate need to be considered. Actual transmissions for our fused quartz plate 1.8 mm thick were taken at two wave-lengths (2540 and 3130A) by means of a thermopile. A smooth curve was constructed which passed through these two points and coincided in the visible region with the transmission curve as calculated from the index of refraction of fused quartz. It was assumed that in the visible region there was no true absorption. The values taken from the curve so constructed are given in Table I.

TABLE I

Energy calibration of the spectrum.

t denotes the fraction of the energy transmitted by the first quartz plate; t' the energy in the tube per unit energy outside when the light goes straight through the tube.

λ (angstroms)	t	t'	Energy (in ergs/sec.)		
			outside	after traversing quartz plate	after reflection from 2nd plate
2399	.805	.869	9.4	7.6	8.16
scattered			6.9	5.6	
2525, -35, -37, -39	.823 (obs.)	.887	33.4	27.4	29.67
2804	.857	.920	17.9	15.3	16.47
2967	.874	.940	23.4	20.4	22.00
3022, -8	.880	.946	41.3	36.3	39.1
scattered			5.2	4.6	
3126, -32, -45	.887 (obs.)	.953	82.3	73.0	78.3
scattered			5.0	4.4	
3342, -52	.900	.963	15.8	14.2	15.2
3650, -56, -63, -80	.916	.979	127.6	116.7	124.8
4047, -78	.927		47.2	43.7	
4348, -59	.930		71.9	66.7	
5461	.931		73.7	68.6	
5769, -90			93.7	87.2	
5804, -19	.931				
6152, 6232	.932		4.3	4.0	

When the light goes straight through the tube and is partially reflected at the second plate the flux of energy through the tube is $t(1 + r + ra^2)$,

[16] Hildebrand, J. Amer. Chem. Soc. **40**, 45 (1918).

where t is the fraction transmitted by the first plate (taken from the curve already constructed), r is the reflection coefficient and a is the fraction transmitted at each face. This second series of values is also given in Table I, which in addition contains calibration of the spectrum taken from Fig. 3.
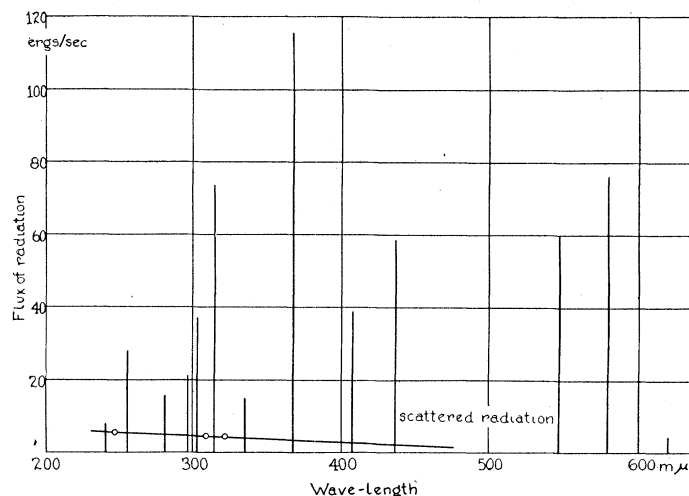

Fig. 3. Flux of radiation from a 225 watt quartz mercury arc 25 mm from a 10.1 by 0.75 mm entrance slit of the spectrograph, after passing through spectrograph. The slant line near the bottom of the figure refers to the scattered radiation.

The last five values in the next to the last column of Table I have been corrected by multiplying by 0.9 to take account of the fact that a different second slit was used in the last part of the experiment which did not cut off the stray light at the top and bottom and a little of the image itself, while it did in the calibration. This column is the one used for the calculation of the efficiency of the photoelectric effect of the caesium-gold alloy. The last column was used in calculating the efficiency of photo-ionization in the caesium vapor.

TABLE II

Ionization of caesium vapor.

Average temperature 166°C; potential of opposite plate $= +3.0$ volts.

Wave-length (Angstroms)	Grid potential (volts)	Current (amp.)	Ions/cc/sec.	Ions/cc/erg	Ions/atom/erg $= B$	Temp. (°C.)
2399	$-.67$	$.88 \times 10^{-12}$	10.87×10^5	13.32×10^4	22.35×10^{-11}	166
2525–35–37–39	$-.67$	2.98	35.4	11.94	20.10	167
2804	$-.67$	1.09	12.08	7.34	12.33	166
2967	$-.50$	3.12	33.65	15.27	25.00	
3022–8	$-.43$	4.68	49.8	12.74	21.40	
3126–32–45	$-.19$	15.37	158.5	20.25	34.10	166
3342–52	$-.19$	.16	1.57	1.03	1.73	166
3650–56–63–80	$-.19$	.84	7.77	.62	1.04	

(b) *Ionization of caesium vapor.* In Table II are shown the results for caesium vapor at 166°C. A run was also made at 203.9°C which gave similar results. These results are not given because of the possibility that the vapor was not saturated. The ionization current in Table II is corrected for the estimated fraction of the light cut off by condensation of caesium on the front quartz plate. In a second run at 203.9°C condensation was eliminated by placing special non-inductively wound heating coils over the two ends of the tube and keeping them about 10° warmer than the body of the tube. The number of ions per cc per sec. is corrected for the grid aperture by dividing by 0.628. The deflections due to the ionization currents ran as high as 103 mm. The number of ions per atom per erg is of course the ionization efficiency or the Einstein probability coefficient of absorption B. The values of B in Table II are estimated to be in error by not more than 5 percent when
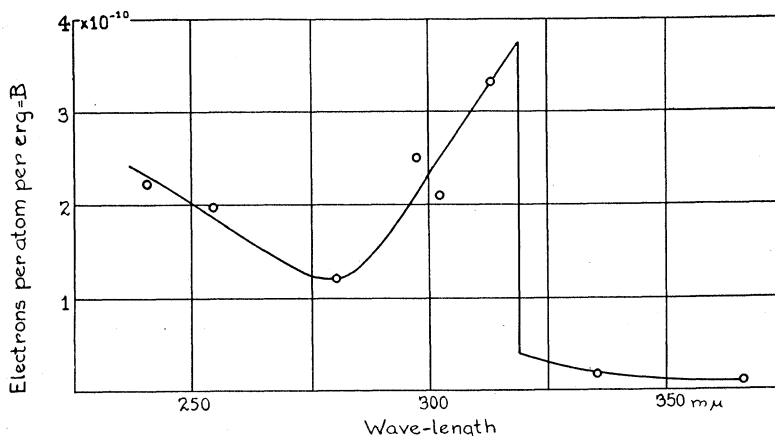

Fig. 4. Ionization efficiency, B, for caesium vapor at 166°C.

relative values are considered, but the possible error in absolute value is probably about 25 percent.

The values of B are plotted in Fig. 4. We have drawn the line vertical at 3184A as we believe it to be. The ionization for wave-lengths greater than this threshold rises slightly to meet the foot of the line. Had it been possible to obtain more points in this region it is probable that the curve would not have been smooth but would have consisted of a succession of peaks gradually rising in height and number as 3184A is approached. This would be accounted for by the completion of ionization of excited atoms by thermal impact. From Fig. 3 it is seen that the spectrograph scattering at 3350A is 5.5 percent of the energy at 3130A. If all the scattered light came from this wave-length all the ionization apparently due to 3350A would be accounted for by the spectrograph scattering. Scattering at 3660A is 4.9 percent of the energy at 3130A and this would account for more than the observed ionization. Of course all the scattered light does not come from 3130A.

The shape of the curve is rather uncertain because this and only one other successful run were obtained before the tube cracked. However, for wave-lengths less than 3184A the shape of the curve checks qualitatively with those of the curves obtained by Mohler, Foote and Chenault and also with the shape of the absorption curves of Harrison. The absolute values of the efficiency are here given for the first time. At 3184A it is seen that the Einstein probability coefficient is about 4×10^{-10} electrons per atom per erg. The minimum occurs at 2800A and is about one-third of the above maximum. Our run at 204°C gave one-fifth and Mohler, Foote and Chenault's results give one-eighth for this ratio of minimum to maximum. Their results were for higher temperatures. This seems to show that the ratio of minimum to maximum decreases with increasing temperature. They also found the minimum to be at about 2800A although at 230°C it seems to be shifted toward shorter wave-lengths. If this is a true minimum and the curve rises
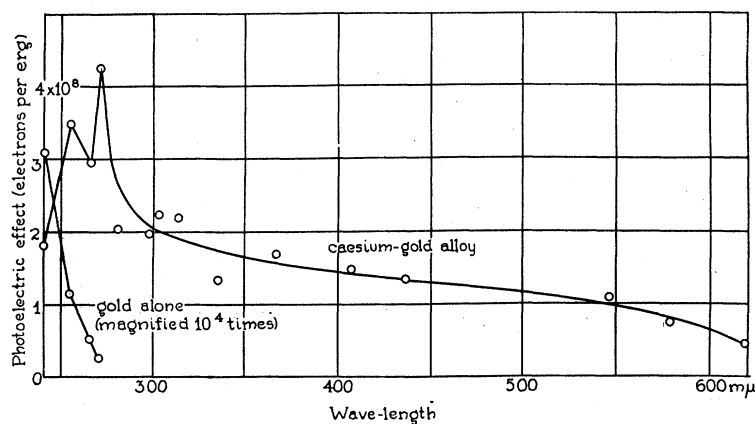

Fig. 5. Photoelectric effect of a caesium gold alloy surface.

again for shorter wave-lengths as our results indicate, then neither a λ^4 nor a λ^3 law could possibly fit.

(c) *Photoelectric effect for caesium-gold alloy.* The first tube made had gold plated electrodes. Because we had trouble with copper chloride fogging the quartz plates when heated after cleaning with HCl, we changed to electrodes made of solid coin gold from Baker. When we finally filled the tube with caesium a drop that had lodged between an electrode and the glass disappeared within a few hours, covering the whole electrode with a light colored alloy. This was at room temperature. When the tube was raised to 200°C very large thermionic currents were observed first in one direction and then another. Upon cooling, the glass was perfectly clean everywhere with no excess caesium in a drop anywhere. The gold was very light colored, indicating that the caesium had readily formed an alloy with it. Since no data on the photoelectric effect of caesium-gold alloys were to be found in any tables a test was run to determine the photoelectric effect, per unit light intensity, of the alloy. The light went slightly obliquely through the

first quartz plate and was carefully directed to the grid. The ionization before the caesium was introduced and then after is plotted in Fig. 5. It will be seen that the current from the gold is about one ten-thousandth of that from the caesium-gold alloy. It seems that despite the precaution of using a liquid air trap, enough mercury vapor got through to make its presence felt. Before the caesium was introduced the current seemed to be entirely due to mercury for it approached zero at the limit determined by Kazda[17] for liquid mercury, namely 2735A. On the other hand it is possible that the limit for gold is about the same as that for mercury. The large hump at short wave-lengths for the caesium-gold alloy is probably due to mercury or gold. The photo-currents from the alloy are about 1000 times the current from 1 cc of vapor at about 200°C. This means that 1 sq. cm of liquid caesium is equivalent to 1000 cc of caesium vapor at 200°C in its absorbing power. The sensitivity of the alloy is rather uniform except near the mercury threshold and thus it could be used as an ultra-violet photometer.

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[17] Kazda, Phys. Rev. **26**, 648 (1925).