THE IONIZATION POTENTIAL OF MERCURY VAPOR AND THE PRODUCTION OF THE COMPLETE SPECTRUM OF THIS ELEMENT.

BY T. C. HEBB.

THE results of Davis and Goucher[1] and of Bishop[2] seem to prove the correctness of the suggestion of Van der Bijl[3] that the apparent ionization of mercury vapor when bombarded with electrons possessing a velocity of 4.9 volts, as observed by Franck and Hertz[4] and by Newman,[5] was due to the photo-electric action of the radiation $\lambda = 2536.7$ acting on the receiving plate of the ionization chamber. Their results are also in harmony with those obtained by McLennan and Henderson[6] and also by Tate,[7] viz., that the ionization potential of mercury vapor is 10.3 volts.

Neither the above suggestion nor the experimental results quoted, however, explain the results obtained by the writer:[8] viz., that the complete spectrum of mercury vapor appeared at 4.9 volts, and that an arc struck at that voltage. Millikan,[9] however, has suggested that the same radiation $\lambda = 2536.7$ acts photo-electrically on the mercury vapor and produces the necessary ionization. If this should prove to be true then the fact will cast some light on the photo-electric action.

If, however, it should be found that photo-electric action is not sufficient to explain the arc at 4.9 volts, it would seem to be necessary to assume that under certain conditions mercury vapor can be ionized by collision with electrons moving with a velocity of 4.9 volts.

The experiments reported in this paper were undertaken in the hope that the above question might be decided. The results obtained will be dealt with under the following five heads: (1) Arcing voltages; (2) Current-potential Relations; (3) Striations; (4) Ionization Potential and (5) Photo-electric Action.

[1] Davis and Goucher, PHYS. REV., Vol. 10, p. 101, Aug., 1917.
[2] Bishop, PHYS. REV., Vol. 10, p. 244, Sept., 1917.
[3] Van der Bijl, PHYS. REV., Vol. 9, p. 173, Feb., 1917.
[4] Franck and Hertz, Deutsch. Phys. Gessell. Verh., Vol. 11, p. 512, 1914.
[5] Newman, Phil. Mag., Vol. 28, p. 753, Nov., 1914.
[6] McLennan and Henderson, Proc. Roy. Soc., *A*, Vol. 91, 1915.
[7] Tate, PHYS. REV., Vol. 7, p. 686, June, 1916.
[8] Hebb, PHYS. REV., Vol. 9, p. 371, May, 1917.
[9] Millikan, PHYS. REV., Vol. 9, p. 378, May, 1917.

1. Arcing Voltages.

The apparatus employed was essentially the same as that used in the previous work on the mercury arc. A horizontal section is shown in Fig. 1. *A* was a glass tube about 20 cm. long and about 2.5 cm. in diamteter. *B* and *C* were iron caps which were fastened to the tube with Khotinsky cement. Through *B* and *C* passed the iron electrodes which carried the anode *D* and the cathode *E*. Pump connections were made at both *F* and *G*, so that in case there was a small leak the resultant air did not have to pass across the arc space *DE*. All the joints were sealed

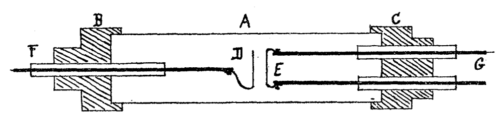

Fig. 1.

with Khotinsky cement. The anode *D* was of platinum foil usually about one centimeter square. The Wehnelt cathode was also of platinum foil .003 cm. thick and about 1.0 cm. in length. Its width was usually about .4 cm. The current used to heat the cathode varied between 10 and 20 amperes. Directly under *D* and *E* the glass tube was expanded into a depression in order to hold the mercury and the expansion was graded from the two ends of the tube, so that as fast as the mercury condensed at the ends it ran back. This kept a constant supply of mercury under the arc DE. The two iron caps, *B* and *C*, were surrounded by cooling vessels through which water circulated. The central part of the tube was surrounded by a gas-heated asbestos furnace with a sheet-iron bottom. The mercury evaporated at the center of the tube and passed both ways to the ends where, as stated above, it was condensed and returned to the center. As a result there should be produced in the region *DE* an atmosphere of the purest mercury vapor. This should be true even though the vacuum produced by the pump was not very high. As a matter of fact the pump used gave a minimum pressure of .25 mm.

With the apparatus as outlined above it was possible for me to substantiate my previous result, viz., that the arc could be caused to strike at a potential difference as low as 4.9 volts. But in doing so I found that it could be caused to strike at any potential difference above 4.9 volts by varying some or all of the following factors: (1) The temperature of the cathode, (2) the temperature of the furnace, (3) the distance between the anode and cathode and (4) the pressure as recorded by a McLeod gauge.

Curve A, Fig. 2, gives the relation between the striking voltage and the amperes through the cathode for a particular case. The McLeod gauge reading was 1.9 mm. In considering this curve it should be noted that the distance between the mercury and the cathode was about one centimeter and hence a rise in temperature of the cathode caused a more rapid evaporation of the mercury. That this made a difference was proved by the observation that the slope of the curve decreased when the mercury was not directly under the anode and cathode.

In regard to the effect of the second factor mentioned above, it may be stated that the striking voltage decreases with a rise in the temperature of the furnace, although I have no exact data to offer.

And in regard to the third factor I found that the striking voltage increased with the distance between the anode and cathode.

Curve B, Fig. 2, shows the relation between the striking voltage and the reading of the McLeod gauge for a particular case. Everything else was kept as constant as possible. It will be noticed that the striking voltage decreases with the pressure, reaches a minimum and then rises again. No significance should be attached to the fact that the curve starts at about 10 volts and rises again to that value. It could have been extended and was in some cases. The minimum point of the curve only reaches the value of 6 volts, but curves could be obtained in which the minimum potential difference had any value above 5 volts.

As a result of my experiments on arcing voltages I have come to the conclusion that the striking of the arc at 4.9 volts depends on (1) the density of the electron stream, (2) the density of the mercury vapor, and (3) the purity of the mercury vapor. If the electron discharge is weak or if the density of the mercury vapor is low, then there will be no arc formed at these low voltages. Further if there is the slightest trace of a foreign gas present, then, even though other conditions are favorable, the arc will not strike as low as 4.9 volts. This last condition is as would be expected if one considers the path of an electron which leaves the cathode and moves towards the anode through a dense atmosphere of mercury vapor. Owing to the elasticity of the collisions between electrons moving with speeds of less than 4.9 volts and molecules of mercury vapor, the electron probably makes many excursions back and forth past a certain point before passing on to the anode. If there were a molecule of an inelastic gas at that point the probability of collision with this molecule and the consequent loss of the electron's energy would be great.

2. Current-Potential Relations.

Using the same apparatus with a low resistance galvanometer in series with the experimental tube I made a study of the current-potential relations in the arc. With this arrangement I found, as would be expected from a consideration of the previous results, that I could get a current-potential curve which took a decided bend at about 5 volts. I also found that by varying the same conditions previously mentioned under Arcing Voltages I could get the bend to occur at any potential

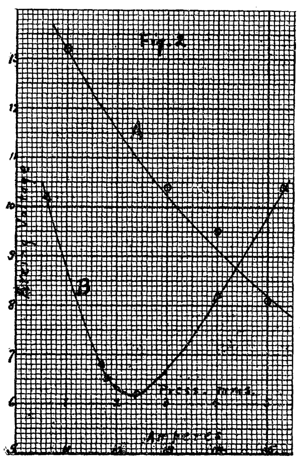

Fig. 2.

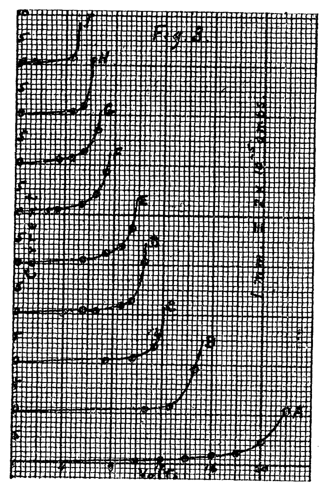

Fig. 3.

difference greater than 5 volts. Fig. 3 shows nine current-potential curves taken for a certain arrangement of the tube. The same cathode was used in all cases with the same current of 20 amperes flowing through it. The distance between the anode and cathode was about 3 mm. In all cases the rapid rise in current led to the striking of the arc. Most of these values were too large to represent on the diagram but they were utilized in getting the shape of the curve. Curves *A*, *B*, *C*, *D* and *E* were produced at pressures of 10, 6, 4.5, 2.2 and 1.3 mm. respectively, as recorded by the McLeod gauge. Everything else was kept constant, but the temperature of the furnace was low. Curves *F* and *G* were produced at the same pressure of .35 mm., but the temperature of the furnace was higher than in the previous cases. In the case of *G* the evaporation of the mercury was more rapid than in the case of *F*. For curve *H* the pressure was 2.7 mm. and the temperature of the furnace was still higher. Curve *I* was produced at a pressure of 5 mm. and at a continued high temperature. I did not determine these curves for the purpose of representing them together and hence the differences between the conditions under which they were taken are quite erratic.

3. Striations.

The conditions in a vacuum tube with a Wehnelt cathode are favorable to the study of striations, and as the striations radiate the complete spectrum of the element they appear to afford a method of studying the minimum voltage necessary to produce this radiation. In order to prevent the arc from striking, however, it is necessary to work with a comparatively cool cathode. I found that a red-hot cathode separated about 5 mm. from the anode gave very satisfactory results when the pressure was from 1 to 3 mm. If, with these conditions and with the temperature of the furnace low, the potential difference between the anode and cathode was raised, light appeared on the surface of the anode. The potential difference at which this occurred was never low, but usually in the neighborhood of 10 to 12 volts. If then the voltage was still further raised, the light on the anode grew towards the cathode and a portion of it separated from the main body of light on the anode. In all cases I found that the increase in potential difference necessary to produce this separation was 5 volts. If after the first striation was formed the potential difference was further increased the phenomenon repeated itself, the first striation in the meantime having moved nearer the cathode. The formation of this second striation also required the addition of 5 volts. The production of each new striation required an extra 5 volts. I have had as high as four distinct striations and the light on the anode with a potential difference of 32 volts. In this case the initial light was produced at 12 volts. On the other hand, with the furnace at a high temperature I have had two striations and the light on the anode for a potential difference of 15 volts.

The difference between the case where the temperature of the furnace is low and the case where it is high probably lies in the purity of the vapor between the anode and cathode. If the temperature is low, then the evaporation of the mercury will not be sufficient to drive away all foreign gases and as a consequence the electrons will lose energy in passing from the cathode to the anode. As a consequence a potential difference greater than 5 volts is required to produce light on the anode. In spite of this loss, however, the addition of 5 volts will make a second ionization possible. In the case where the furnace was at a high temperature, however, the evaporation of the mercury was sufficiently rapid to drive away all foreign gases and as a consequence the electrons lost no energy, other than that due to ionization, in passing from the cathode to the anode.

In connection with striations it may be of interest to state that I have had them so close together and so close to the cathode that I could only see the faintest dark line separating them.

4. Ionizing Potential.

It was considered both of interest and of value to determine the ionizing potential of mercury vapor under conditions somewhat similar to those in the preceding experiments, that is, to determine the ionizing potential in an absolutely pure atmosphere of mercury vapor having a pressure of one or more millimeters. In order to make this determination the anode of Fig. 1 was replaced by an ionizing chamber. The chamber consisted of a platinum cylinder about 4 cm. in length and 1.5 cm. in diameter. The end of the cylinder near the cathode was covered with platinum foil containing three slits. The central slit was about 1 cm. in length and about .3 cm. in width. The others were somewhat smaller. A small receiving disk was placed about 2 cm. from the cathode end of the cylinder. The cathode was separated 1–3 mm. from the end of the cylinder. Mercury stood under both cathode and ionization chamber and the apparatus was heated as usual. The ionization chamber was kept charged to a constant positive potential of 24 volts. The cathode was charged to a positive potential of less than 24 volts and hence the electrons were accelerated as long as they were between the cathode and ionization chamber. As soon, however, as they got inside of the chamber they were retarded.

The gold-leaf electroscope was set to a sensitiveness of about .05 volt per division. There was a condenser in parallel with it and the two together—condenser and instrument—had a capacity of about 230 e.s.u. With it, therefore, it was possible for me to measure currents as large as 10^{-9} amperes, when charging it to 5 volts. I was not able, however, to measure very small currents accurately, for I found that the passage of the mercury vapor over the receiving disk charged it positively. This was reduced to a minimum by arranging the apparatus so that the receiving disk was near the center of the furnace. But even under these conditions many observations were vitiated, apparently, by a sudden rush of vapor.

The results plotted in curve A', Fig. 4, were taken without the use of the capacity mentioned above. The McLeod gauge registered 1.2 mm. The distance between the anode and cathode was 1.0 mm. The cathode was new and uniformly coated with BaO and was heated by a current of 19.5 amperes. The current flowing between the anode and cathode varied from 14×10^{-5} amperes at 4.5 volts to 23×10^{-5} amperes at 5.3 volts. The minimum potential difference between anode and cathode has been used as abscissa. It is quite evident that ionization must have started at about 4 volts, and as the drop in potential along the cathode was .8 volt the ionization potential must have been in the vicinity of 4.8 volts.

The results obtained with an old cathode are sometimes very marked due to the fact that the BaO wears down to narrow patches at either end of the cathode. Curve *B'*, Fig. 4, was plotted from data taken with such a cathode. The McLeod gauge reading was .85 mm. It will be noticed that the curve is very steep. As a matter of fact the ionization current increased over one hundred times when the potential difference between the anode and cathode was changed from 3.9 to 4.0 volts. It was possible to estimate quite closely the potential drop in the cathode at this point and this value—.9 volt—added to 4.0 volts gives 4.9 volts.

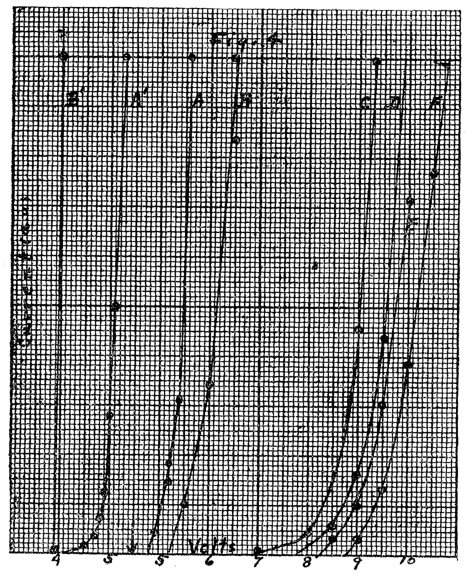

Fig. 4.

The curves shown—*A'* and *B'*, Fig. 4—are similar to those obtained by other experimenters but I do not believe that the results can be explained on the assumption that the radiation $\lambda = 2536.7$ has acted photo-electrically on the receiving plate of the ionization chamber. Although such an action must have existed, the current produced by such action in these experiments must have been very small compared with the currents measured. This was especially true as the receiving plate had an area of only .25 square centimeter. And even when the receiving plate consisted of a small platinum wire sealed in glass it was found that the ionization current was still large.

Although ionization of mercury vapor occurred at 4.9 volts under favorable conditions, as shown above, it was also possible to get it to occur at any potential difference above 4.9 volts. This was accomplished by simply varying the temperature of the furnace. Some results are shown in Fig. 4—Curves *A–F*. The data for these curves were taken with a constant current of 16.5 amperes through the cathode. The latter was separated about 1.5 mm. from the anode. The pressure indicated by the McLeod gauge was constant at .8 mm. The temperature of the furnace, however, was progressively lower, beginning with curve *A*. The gap between *B* and *C* could have been filled with similar curves had it been desired. The data for the curves *C–F* were taken as the temperature of the furnace was gradually lowering. This accounts to a great extent for the tendency of the curves to bend to the left as they approach the P.D. axis. The abruptness with which the curves drop into the P.D. axis is very pronounced in some cases. For example, in one case the ionization current at 10.8 volts was too small to be detected, if it existed at all. When, however, the potential difference was increased to 11 volts, the ionization current became about 10^{-9} amperes.

These results appear to me to prove that in order to get ionization of mercury vapor at 4.9 volts under conditions similar to those in my experiments it is necessary to have the vapor absolutely pure.

5. Photo-Electric Effect.

The previous experiments seem to prove conclusively that there is a distinct and pronounced ionization at 4.9 volts. But this ionization may be due to photo-electric action in a manner suggested by Millikan.[9] Further than that the results of Davis and Goucher[1] and also of Bishop[2] would appear to prove that such was the explanation. But even if some such action as Millikan suggests took place, it does not seem possible that the effect would be large enough to explain the results. It does not seem possible that radiation which required two or three hours to effect a photographic plate could produce 10^{-9} amperes photo-electrically as I have measured. Nor does it seem probable that the same radiation, even by the reciprocal action suggested by Millikan, could cause such large increases in the arc currents as I have obtained. For instance, in one case the current flowing between the anode and cathode changed from 10^{-5} amperes at 5 volts to 40×10^{-5} amperes at 5.5 volts without the production of an arc. And in the following case where the arc struck the increase was much greater. In this case the current changed from 3×10^{-5} amperes at 5 volts to 540×10^{-5} amperes at 5.3 volts. Still another objection to the theory, it appears to me, is the fact that striations can be obtained in mercury vapor and especially in such close proximity to one another.

However, in order to test whether the photo-electric action was the cause of the ionization I arranged a mercury arc in air directly outside of the experimental tube and so arranged that its light passed into the front end of the ionization chamber. The experimental tube had been exchanged for one of quartz. Conditions were then arranged so that a large ionization current was produced by the electrons from the cathode. The voltage between the anode and cathode was then reduced to zero and the mercury arc in air started. It was found that the photo-electric current produced by the 4-ampere arc was, in some cases, equal to the current produced by the electron stream. Thus in one case at a pressure of 2.9 mm. and with 5 volts between the anode and cathode the electroscope charged up to 2.5 volts in 4 seconds. The voltage between the anode and cathode was then reduced to zero and the mercury arc in air started. The latter produced exactly the same ionization current. A carbon arc produced no results. As the effective radiation produced by a 4-ampere arc must be hundreds of times greater in intensity than the radiation $\lambda = 2536.7$ produced in the experimental tube by the electron discharge due to 5 volts, it does not seem probable from this result that the ionization produced by the 5 volts could have been due to the radiation $\lambda = 2536.7$.

It was further found that changing the pressure in the tube had very little effect on the ionization produced by the arc whereas the same changes caused the ionization current produced by 5 volts to vary from zero to a large value.

I also tried to find what effect the mercury arc in air had upon the striking voltage of the arc in the vacuum. Conditions were arranged so that the arc in the vacuum struck at 8 volts. The voltmeter was then

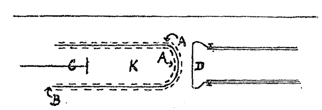

Fig. 5.

set at 7.9 volts and the mercury arc in air started. If it sets up ionization in the tube of sufficient amount, then one would expect the arc in the vacuum to strike lower than 8 volts. No such effect was observed.

The ionization chamber was then arranged as in Fig. 5.

Two platinum cylinders AA were separated by a quartz test tube B and together with C as a receiving plate constituted the ionization chamber. A and A were joined electrically and a potential difference of 24 volts was applied. No electrons from the cathode D could get into the ionization chamber K. Mercury was kept in the chamber K as well as under the arc *DA*. The current flowing between the anode and cathode was measured and hence I could tell when ionization began. Some of the radiation produced should pass into the chamber *K* and produce ionization. Of course some of the radiation was absorbed by the quartz test tube which was about 1 mm. in thickness and some was absorbed by the mercury vapor which formed an unavoidable layer between two cylinders *AA*. This layer was about .5 mm. in thickness. As mentioned before the passage of mercury vapor over the receiving plate *C* causes it to be charged with positive electricity. I could not obviate it in this case as in the previously mentioned one and hence it was not possible for me to detect extremely small currents but in no case did I detect any current due to the radiation $\lambda = 2536.7$. That the apparatus would have responded as expected if the radiation $\lambda = 2536.7$ had produced ionization in sufficient quantity was proved by the fact that the slightest arc between *D* and *A* produced a rapid charging of the electroscope. My experiments along this line, therefore, have not shown, so far, any evidence of an ionization of mercury vapor by the ratiation $\lambda = 2536.7$.

Summary.

1. These experiments prove conclusively that mercury vapor may be ionized when bombarded with electrons moving with a velocity acquired in falling through 4.9 volts and that the complete spectrum of mercury is produced as a result.

2. Experimental evidence is given to show that this ionization is not produced by the radiation $\lambda = 2536.7$ acting photo-electrically on the mercury vapor.

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