Second Series *November, 1920* *Vol. XVI., No. 5*

THE

PHYSICAL REVIEW.

ARCING VOLTAGES IN MERCURY VAPOR AS A FUNCTION OF THE TEMPERATURE OF THE CATHODE.

BY T. C. HEBB.

SYNOPSIS.

Low Voltage Arcs in Mercury Vapor.—One of the objects of this work was to study the production of the low-voltage arcs in a more uniform mercury-vapor atmosphere than had been used before. As a result of improved apparatus much more consistent results have been obtained. It has been shown that there is a linear relation between the striking voltage and the current through the cathode for the larger currents. This in turn has been shown, in the case of platinum coated with lime, to mean that the striking voltage forms a linear relation with the temperature of the cathode. The results further suggest that the difference between the potential at which ionization takes place and the accepted ionization potential is directly proportional to the absolute temperature. *Results with Tungsten Cathodes.*—In line with the above it has been shown that tungsten cathodes produce lower arcs than lime-coated platinum cathodes. A striking voltage as low as 3.2 volts was obtained, the lowest for platinum coated with CaO having been in the vicinity of 4.9 volts. *Effect of Thickness of Oxide Deposit on the Cathode.*—It has been shown that the thickness has an effect on the value of the striking voltage. A thinly coated platinum cathode produced an arc at a potential as low as 6.0 volts whereas a thickly coated one produced an arc as low as 4.9 volts. *Effect of Hot Anode.*—A hot anode used with a thinly coated platinum cathode has been found to produce a lower arc than when the anode was not heated. *Discussion of Results.*—The results are briefly discussed but no definite theory is offered to explain them.

IN two previous papers[1] I have shown that mercury vapor can be ionized at potentials as low as about 5 volts. These results which were somewhat contradictory to those of McLennan and Henderson[2] have since been substantiated by McLennan.[3] As the type of apparatus used in my previous experiments was considered unsatisfactory for the better understanding of the relations between the various factors involved

[1] PHYS. REV., Vol. 9, p. 686, 1916, and Vol. 11, p. 170, 1918.

[2] Proc. Roy. Soc., A, Vol. 91, 1915.

[3] Proc. Phy. Soc. Lon., Vol. 31, Dec., 1918.

in the production of the low ionization, I have constructed and used the following apparatus.

The glass tube *A*, Fig. 1, about 2.5 cm. in diameter, was cemented with Khotinsky cement to the base *BB* which stood on the shelf *SS*. Through the plug *P* three holes were bored—one to admit the barometer tube *t* and the other two to admit two electrodes for conveying the current to the cathode *c*. The anode, *a*, was attached to an aluminum cylinder which was inserted in the side tube *m*. Electrical connection was made between the anode and the mercury in the tube *R* by a platinum wire which passed down the tube *U*. The apparatus could be evacuated through the tube *U* as indicated in the figure. The upper part of the apparatus was surrounded by an asbestos furnace containing a glass window. The furnace was heated electrically. By the use of this apparatus a uniform mercury-vapor atmosphere could be obtained around the anode and cathode. The pressure of this vapor could be obtained by raising the reservoir *Y* until the mercury stood in the tube *U*. The apparatus was evacuated by means of a Toepler pump and the pressure of the remaining gas was measured with a McLeod gauge. During the process of "heating up" of the apparatus and of the cathode a great deal of gas was given off. Pumping was continued, however, until the pressure was of the order of .001 cm. In order to obviate the collection of this gas in the apparatus *A*, the mercury in *R* was not allowed to shut off the tube *U*. As is evident, the evaporation of mercury in the tube *A* and its passage out through *U* rapidly clears the tube *A* of any foreign gases. The thermometer *T* had its bulb placed below the level of the surface of the mercury in *A* and very near the outside of the tube.

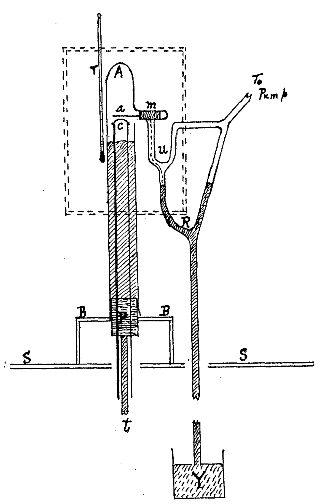

Fig. 1.

The cathode, unless otherwise stated, was of platinum foil about .0025 cm. in thickness. Various widths were used but the length was about 2.0 cm. Either CaO or SrO was placed on it. The anode *A* was either platinum foil or platinum wire.

It was soon found that much more consistent results could be obtained with this apparatus than with the previous type. With my earlier apparatus I found that it was necessary to have the pressure, as read by a McLeod gauge, at a particular value in order to get the lowest arcs and that a greater or less pressure increased the value of the arcing voltage. With the present form I found that the pressure of the mercury was of less importance. It still had to be above a certain minimum value but, aside from that, no great care had to be exercised. If the thermometer read anywhere between 170 and 220° C. the results were practically the same. This gave a vapor pressure of the order of 1–3 cm. of mercury.

As in the previous work so here it was found that the electronic density was important. Low temperature cathodes would not give low arcs. As the temperature of the cathode rose, however, the striking voltage dropped rapidly until a further increase had only a small effect on the striking voltage. This is brought out by Fig. 2 which gives the results

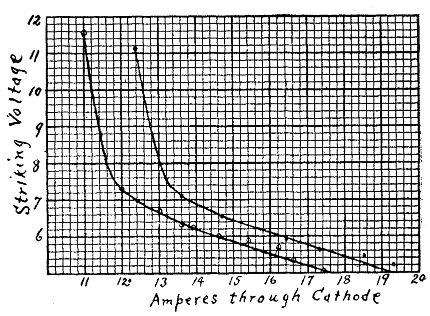

Fig. 2.

for two different cathodes rather heavily coated with CaO. I mention the thickness of the CaO coating as I am of the opinion that it makes a difference. In my previous work on the mercury arc I used heavy coats of BaO on the cathode.

It will be noticed that the lower parts of the graphs approximate more or less to straight lines. The straightness of this part of the graphs I have examined closely and find that in a great many cases it seems to be straight within the limits of observation. Had I taken care to glow well the cathodes used in Fig. 2 before I made those observations the lower part of the graphs, I have no doubt, would have been straight.

In order to obviate the correction and uncertainty due to the drop in the cathode I arranged a revolving commutator so that the cathode was heated intermittently, and the potential between the anode and cathode was applied only when the cathode current was off. In the use of the commutator the greatest care was exercised to prevent the potential being applied even for an instant while the cathode current was flowing. The current was made and broken 60 times per second and the potential was applied a like number of times. This method is not favorable for studying the weak arcs produced with low temperature cathodes hence that end of the graph is not shown. Fig. 3 gives the results obtained with such a commutator when the cathodes were rather heavily coated with CaO. The two graphs are for separate cathodes.

The graphs of Fig. 3 suggest that there is no significance, as far as these experiments go, in the potential difference of 4.9 volts. As a matter of fact it was only on rare occasions that I got an arc as low as 4.9 volts with the present apparatus. And it should be stated that in

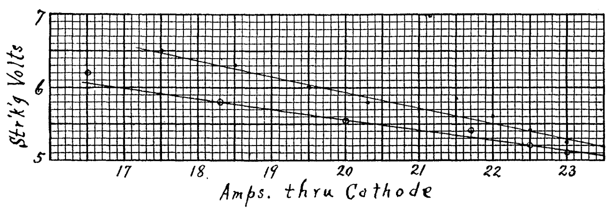

Fig. 3.

the experiments recorded in Figs. 2 and 3 the cathodes were heated until they melted.

The graphs in Fig. 3 also suggest the idea that if the current could be still further increased the striking voltage would keep on decreasing in a linear manner with the current. I attempted to follow this line of reasoning by using tungsten coated with CaO but owing, apparently, to a chemical change between the tungsten and the CaO I was unsuccessful. With tungsten alone, however, I found that I could get the arc to strike at voltages much lower than I had obtained before. I am not prepared at present to say what is the lowest voltage at which an arc in mercury vapor using a tungsten cathode can be made to strike but I have got it as low as 3.2 volts. This was obtained with the commutator so that there is no uncertainty from cathode drop. Further I found that there was a linear relation between the current through the cathode and the striking voltage as was the case for platinum cathodes. It should be stated that the tungsten used was in the form of a strip as nearly as possible to the size of the platinum used. Fig. 4, graph *a*, shows the results for one cathode. Although only three observations were made before the cathode melted, it will be seen that they lie very close to a straight line. With the commutator I have found it impossible to make observations on arcs when I used low-temperature cathodes. Fig. 4, graph *b*, however, gives the results with a tungsten cathode heated without the use of the commutator. In order to approximate the correction for cathode drop the cathode was constricted at the center so that only that portion of it was highly heated. It will be noticed that the upper portion of the graph is very steep, as was the case for platinum, and that then the graph becomes straight. The lowest striking potential observed was 3.9 volts but the cathode melted at about 30 amperes before other observations were made. If the straight

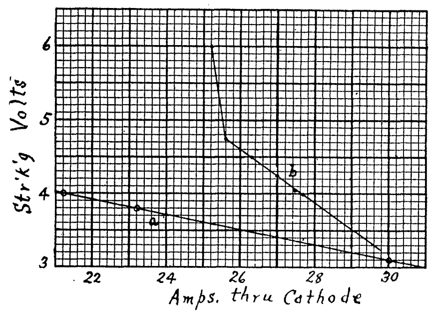

Fig. 4.

portion of the graph is produced, however, it reaches about 3.2 volts at 30 amperes.

I have already suggested that the thickness of the oxide deposit on the cathode affected the value of the striking voltage. I had always followed the practice, unusual I think, of coating the cathode rather heavily. This was done by putting small pieces of the nitrate on the cathode and then heating them. In endeavoring to determine the effect of impurities in the oxide on the value of the striking voltage I was led to use much thinner deposits. I found immediately that there was a considerable change. In fact, it was found that the lowest striking voltage for thinly coated cathodes was in the neighborhood of 6.0 volts. This is shown in Fig. 5 which gives the data for two separate cathodes.

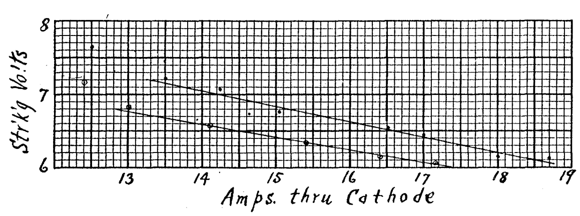

Fig. 5.

In both cases the current was increased until the cathode melted. The two curves also show the variation caused by different treatment of the cathodes. In the case of the upper graph the cathode was used for the first time, whereas in the case of the lower graph the cathode had previously been heated to a high temperature and well freed of gas. In neither case was the commutator used but as only a small spot of CaO was used a fairly close correction for drop in the cathode could be made.

Fig. 6 gives a comparison between the results obtained with two cathodes, one more heavily coated with oxide than the other. The two cathodes were initially of as nearly the same dimensions as they could be made. The commutator was used in both cases. The thinly coated one melted at about 25 amperes whereas the more heavily coated one melted at 27 amperes. In the latter case when the current was first brought to 27 the striking potential was 5.5 volts but as time elapsed the striking potential dropped lower and lower until it reached the minimum of 4.8 volts. Shortly afterwards the cathode melted.

In some cases with coated cathodes the low striking voltage is only temporary. In one particular case, for instance, while studying the effect of vapor pressure on the striking of the arc, the arc suddenly

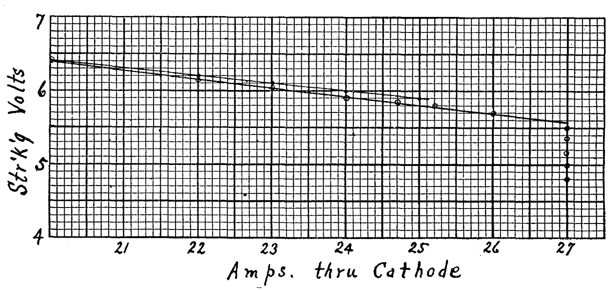

Fig. 6.

began to strike lower and lower until it reached 4.8 volts. The next day I obtained with the same apparatus a minimum of 5.8 volts just before the cathode melted.

The graphs given in Figs. 2–6 show quite conclusively that for the higher temperatures and for the cathodes used the striking voltage is a linear function of the current through the cathode. As the cathode current itself is not the important factor, these results suggested that there might be a simple relation between the striking voltage and the temperature of the cathode. Rough experiments in which I used the melting points of various salts and metals convinced me that the temperature of the cathode was, at least roughly, a linear function of the cathode current. It may be of interest to state in passing that the same apparently holds quite closely for a platinum wire in free air. This will be seen if the results of Langmuir given on page 413, Vol. 34, 1912, of the

Physical Review, be plotted. The article referred to is on the conduction and convection of heat in gases.

To measure the temperature of the cathode more accurately I determined the resistance of a portion of it at two known temperatures, and then made use of the fact pointed out by Langmuir that the temperature-resistance graph for platinum is straight above 1100° C. As I found that I could use the melting points of NaCl and K_2SO_4 most satisfactorily, I used these two temperatures, viz., 801° C. and 1070° C., and drew a straight line through them. This, of course, gives too low a value of the temperature for points above 1100° C. To correct for this, approximately, I drew another straight line between 1070° C. and a point which was 20° C. above the first line at 1900° C. This correction would vary somewhat with the platinum used but seemed from a study of the temperature-resistance curve for platinum to be somewhere near the truth.

The resistance of the portion of the cathode used was determined by measuring the current through the cathode with a standard 0.1 ohm resistance and a potentiometer, and the drop across the portion used with a potentiometer. For the latter purpose two fine pin holes were made in the central part of the cathode about 0.5 cm. apart. Through these holes fine wedge-shaped strips of platinum foil were inserted until they were tight. The ends of these strips were cemented with platinum chloride to platinum wires and these wires led to the potentiometer set. The part of the cathode between the potential leads seemed to have a fairly uniform temperature. Small bits of fused sodium chloride and potassium sulphate were then used to find, in the usual way, the resistance of the cathode at their melting points. The results obtained for one cathode are given below:

Substance.	Amperes.	Volts.	Resistance.
NaCl............	4.652	.2422	.05206
"	4.636	.2400	.05177
"	4.675	.2432	.05204
"	4.656	.2433	.05226
			Mean .05203

Substance.	Amperes.	Volts.	Resistance.
K_2SO_4...........	5.710	.3513	.06152
"	5.737	.3529	.06151
"	5.700	.3511	.06160
"	5.714	.3515	.06152
			Mean .06154

With these two resistances and their respective temperatures the temperature-resistance graph was obtained as indicated above.

Having obtained the above data a small thin spot of CaO was placed at the center of the cathode. This no doubt changed the temperature-resistance characteristics of the cathode, but the method was deemed better than the one in which the graph was obtained after the CaO was placed on the cathode. Of course, it was impossible to use the commutator in determining the striking voltage for any particular temperature and hence an uncertainty is introduced in correcting for cathode drop. As the spot of CaO was placed at the center, the correction was always taken as equal to one half the drop over the cathode. The following table contains the data obtained for the cathode whose resistance-temperature data was given above. The cathode was well heated before these observations were made.

Amps. Thro. Cathode.	P. D. Volts.	Resist-ance	Temp. of Cathode.	Obs'd Str'k'g Voltage.	Cathode and Lead Drop.	Corrected Str'k'g Volt.
6.197	.4433	.0716	1630 K	6.25	1.81	7.16
6.519	.4757	.0729	1670 "	5.90	1.95	6.83
7.046	.5313	.0754	1740 "	5.50	2.15	6.58
7.703	.6036	.0783	1818 "	5.15	2.40	6.35
8.210	.6632	.0807	1890	4.85	2.59	6.15
8.576	.7017	.0818	1925	4.70	2.72	6.06

The cathode melted shortly after the last observation was made. Both amperes and volts were observed with the aid of the potentiometer sets and are more accurate than necessary. The resistance has been calculated with a slide rule.

The relation between the temperature of the cathode and the striking voltage is shown in Fig. 7, lower curve. The upper curve is from data obtained with an entirely different athode. Both graphs show that there is a linear relation between the temperature of the cathode and the striking voltage of the arc. I have not data enough yet to say whether or not these two graphs should be coincident but there is a good possibility that such should be the case as the errors arising from cathode-drop correction, temperature determination and effect of CaO thickness might easily, I think, explain the difference. If these two lines be extended to cut the $T = O$ axis they do so at $V = 11.2$ and $V = 14.0$ volts respectively. These two values are sufficiently close to the ionization potential of mercury vapor, viz., 10.5, to be, at least, suggestive.

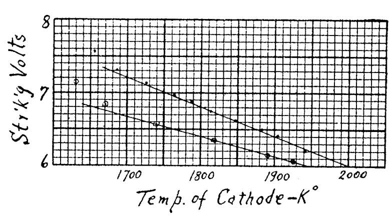

Fig. 7.

I have already pointed out that the lowest striking voltage for mercury vapor with a platinum cathode thinly coated with CaO is in the neighborhood of 6.0 volts. The data I have at present suggest a slightly higher value. And I have also pointed out that the striking voltage for mercury vapor with a tungsten cathode near its melting point is 3.2 volts. If these two voltages be plotted against their corresponding absolute temperatures, viz. 2028 and 3540, and the straight line drawn through them be produced to cut the $T = 0$ axis a value of 9.8 volts is obtained. This value is not very different from the ionization potential of mercury vapor.

Now these data, admittedly imperfect, show that there is a linear relation between the striking voltage of the arc in mercury vapor and the temperature of the cathode for the higher temperatures. They further suggest that the decrease in the ionization potential is directly proportional to the absolute temperature, *i.e.*, that the relation between the striking voltage and the absolute temperature of the cathode can be expressed by the equation $V = 10.5 - kT$, where k is a constant. If the values for V and T at the melting point of tungsten be substituted in this equation a value of k is obtained viz., .0021 volts/degree.

These results do not seem to admit of any simple explanation although at first sight they appear to do so. The fact that the decrease in the potential at which ionization takes place appears to vary directly with the absolute temperature of the cathode suggests that this decrease is due to the velocity of emission of the electrons. Although it has been shown that the velocity of emission of the electrons is directly proportional to the absolute temperature, yet it has also been shown that the velocity is that of thermal agitation and hence would not be equivalent to more than a fraction of a volt at the temperatures used.

As the mercury vapor in contact with the cathode must be very nearly at the temperature of the cathode, it is evident that the absolute temperature of the former would be directly proportional to the decrease in the striking voltage. But the same objection holds for this case as held for the previous one. The increase in the energy of thermal agitation of the molecules per degree is only about one sixteenth of the energy increase necessary to explain the phenomena.

A few experiments were performed to ascertain if possible whether the cause of the low arc depended on the temperature of (1) the cathode, (2) the vapor, or (3) the anode. For this purpose the minimum striking voltage, *i.e.*, the striking voltage just before the cathode melts, was determined for cathodes of widths varying from approximately 0.5 mm. to 7.0 mm. These experiments led me to believe that there was no relation between width of cathode and the striking voltage. The values obtained for all cathodes with thin spots of CaO on them were in the neighborhood of 6.0 volts. As the wider cathodes required very much larger currents to heat them, this would appear to show that it is the temperature of the cathode which is important and not that of the vapor or anode. As, however, no temperature determinations were made these experiments are not conclusive.

Some further experiments were made with a hot anode. For this purpose two commutators connected to the same revolving shaft were used. By this means the anode and cathode could be heated simultaneously and the voltage between the anode and cathode could be applied when no current was passing through either anode or cathode. Further by opening the appropriate switch the anode could be kept cool while the cathode was still heated. The only experiments I have performed with this arrangement of apparatus were those in which I used platinum electrodes. The cathode contained a small thin spot of CaO at its center and was separated 2–3 mm. from a clean platinum anode. Under these conditions I found that with the anode hot the striking voltage was in the vicinity of one volt lower than when the anode was cold. The following data may make it clearer:

Striking Voltage with Anode Cold.	Striking Voltage with Anode Hot.
6.8	5.4
6.5	5.2
6.3	5.15
6.25	5.05

It may be necessary to point out that the different striking voltages with the anode cold were obtained by passing different currents through the cathode.

From these data it will be seen that the heated anode causes a lowering of the striking voltage of about 1.3 volts. Further experiments on these very interesting phenomena developed the fact that although the striking voltage was lowered by the hot anode the amount of lowering was increased by shutting off the current through the anode. Parenthetically, I may add that I think that this effect is due to the change in density of the mercury vapor between the anode and cathode. This state of affairs, however, lasted only a short time and then the striking voltage gradually rose to its old value. Thus with the anode cold the arc struck at 6.7 volts in a certain experiment. The anode was then heated and the arc struck lower (I have not recorded the value in my notebook), but it struck still lower, viz., at 5.05 volts, immediately after the anode current was shut off. The striking voltage then rose slowly to 6.7 volts. It was found that the amount the striking voltage was lowered increased with the temperature of the anode. Also, within limits, a short period of heating did not cause as low an arc as a longer period. Continued heating beyond a certain maximum of time did not further affect the striking voltage. Continued low heating did not accomplish as great a drop as continued high heating. The lowest striking voltage I obtained during the above experiments was 4.95 volts. It will be noticed, therefore, that a platinum cathode with a thin patch of CaO on it can, with the aid of a hot anode, produce an arc about as low as I have obtained with a thickly coated cathode without a hot anode. Whether these two phenomena are produced by the same causes or not, I am unable to say.

At this point I was forced to drop the experiments for a considerable time but it was thought that the results would be of interest even in this unfinished state.

The results embodied in this paper do not appear to me to have any simple interpretation. As long as the striking of the arc was obtained at a value equal to or higher than 4.9 volts it seemed possible that Van der Bijl's theory of multiple collision in terms of the Bohr atom might be the correct explanation. But even this explanation has been shown by Compton[1] to be doubtful. That the density of the electron stream is very important I have shown previously. This is also shown by Fig. 2. As the temperature of the cathode rises from red heat the striking voltage drops rapidly at first as would be expected if density of electron emission is important. But for the lower part of the graph entirely different phenomena seem to be operating. For this part of the graph it seems possible that space charge might be influencing the results but, if so, apparently in no simple manner. When the arc strikes, the operating voltage is still lower, which is also in line with the idea that space charge is active in these phenomena. In this connection I may state that I have had an arc operate with tungsten cathodes as low as 1.7 volts.

In order to explain the striking of the arc at potential differences considerably lower than 4.9 volts and possibly for the explanation of low-voltage arcs it would seem as if one would be forced to assume inelastic collision and gradual accumulation of energy in the atom.

There are other factors, however, which, I believe, have to be considered, such as contact potential difference and impurities. I have previously shown that if sodium or potassium are present with mercury the arc strikes and operates lower than with pure mercury and that the

[1] PHYS. REV., Feb., 1920.

lines of the sodium or potassium may not appear. I have also tried putting a little sodium hydroxide or potassium hydroxide with the CaO on the cathode. The sodium hydroxide causes the arc to strike at 5.0 volts whereas the potassium hydroxide causes it to strike lower than 5.0 volts. In the first case the D lines of sodium appear with the mercury lines, in the latter case only the mercury lines appear.

The results with the hot anode suggest that something in the nature of an impurity has been evaporated from the anode, and hence changed the contact potential. The fact that it takes some minutes for the striking voltage to regain its former value when the anode current is shut off would lead one to think that some deposit is accumulating on the anode. It may be, however, that the extra heat has changed the internal energy of the mercury atoms. I have tried, also, to picture a redistribution of current in the cathode due to the heat from the anode. As the hot lime has a negative temperature-resistance coefficient it might be possible for the calcium oxide to carry more of the current when heated by the anode and hence be at an even higher temperature than the platinum of the cathode. If such is possible this would also explain the lower arcs obtained with thickly coated cathodes. However, even if this were found to be true it would not be an explanation of the production and operation of these low arcs.

UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER, B. C.