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STUDIES ON THE LOW-VOLTAGE ARC IN MERCURY VAPOR AND ITS RELATION TO FLUORESCENCE.

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ABSTRACT.

Low-voltage arc in mercury vapor.—(1) *Variation of the striking and breaking voltages with conditions.* Using a simple tube, with incandescent tungsten filament as cathode and nearby mercury surface as anode, the arc was found to strike at voltages as low as 4.4 and to persist down to 1.8 volts, if the pressure was from 2–5 mm. and the cathode was sufficiently hot. (2) *Explanation.* If, however, correction is made for the initial velocity distribution of the electrons, the minimum electron energy necessary to maintain the arc comes out 5.5 volts which is the difference between the ionization potential, 10.4 volts, and the resonance potential 4.9 volts. Ionization is then effected by two successive mpacts, at 4.9 and 5.5 volts, in agreement with the theory of K. T. Compton. (3) *Effect of the absence of freshly distilled mercury vapor.* When a nickel anode was used and the mercury surface was removed to a considerable distance, 70 to 180 cm., the arc could not be maintained at a net voltage of 5.5, but 6.7 volts was required. This fact was demonstrated with three pieces of apparatus. This indicates that while freshly distilled mercury vapor, as is well known, is particularly active in fluorescent absorption of λ 2536 radiation (4.9 volts), old vapor is more responsive to λ 1849 radiation (6.7 volts).

Correction for initial electron velocities in low-voltage arc measurements.—The difference between the theoretical and observed minimum striking voltages, 2.5 volts for *sodium* (Wood and Okano) and 2.0 volts for *helium* (Compton, Lilly and Ohmstead), is doubtless equal to the voltage equivalent to the minimum initial energy of the electrons which start the arc. A table is given from which the proportion of electrons having energies above any value for any filament temperature may be computed.

INTRODUCTION.

IN spite of the extensive work by various investigators[1] on low voltage arcs in metallic vapors, of which mercury is typical, the question as to whence comes the energy requisite to produce ionization at voltages less

[1] Hebb, PHYS. REV., 9, p. 371, 1917; 11, p. 171, 1918; 12, p. 482, 1918; McLennan, Proc. Phys. Soc. London, 31, p. 1, 1918; Tate, PHYS. REV., 10, p. 81, 1917; Tate and Foote, Phil. Mag., 36, p. 64, 1918; Rognley and Mohler, PHYS. REV., 13, p. 59, 1919; Foote and Meggers, Phil. Mag., 40, p. 80, 1920; and others.

than the minimum ionizing potentials remained unanswered until very recently. While the critical potentials at which the transition from elastic impacts of electrons with mercury molecules to inelastic ones takes place were proved by Franck and Hertz,[1] and later by Davis and Goucher[2], to be definite and determinative values given by the quantum law $eV = h\nu$, the existence of the single lined spectrum λ 2536 to the exclusion of all others was questioned by Professor Millikan[3] from consideration of Kossel's relation. In the light of the then existing experimental data of Hebb,[4] Professor Millikan attributed the striking of the arc at a potential difference of about 5 volts to ionization by electrons emitted photoelectrically by the radiation λ 2536, which is due to 4.9 volt impacts of the primary electrons. That the photoelectric effect is entirely inadequate to account for the observed phenomena was shown by Professor Compton.[5] Nor was Van der Bijl's[6] idea of direct successive impacts entirely successful, for then it would be necessary to assume that the atom could retain its resonance radiation for a length of time many times greater than would correspond to any value of this damping constant which has been found for any substance by direct experiment.[7,8] It was not until the theory of ionization by cumulative action of absorbed radiation and direct impact was proposed and developed by Professor Compton[9] in a series of papers that we have had an explanation of these phenomena which appears to be adequate.

Even then there was a great difficulty. In his recent work Hebb[10] has shown that an arc could be maintained in mercury vapor at as low as 3.2 volts, and in the work described below the lowest maintaining voltage reaches the value of 1.8 volts. Indeed, Hebb was led to doubt the fundamental importance attached to the point of 4.9 volts. It will be shown however, that the position which the point of 4.9 volts occupies in the electronic scheme of the mercury atom is in no way challenged by the maintenance of arcs at such abnormally low voltages; nor is it a fatal objection to the theory of ionization by cumulative action, *provided we take into account the distribution of the initial emission velocities of electrons*

[1] Franck and Hertz, Verh. d. Deutsch. Phys. Ges., 10, p. 457, 1913; 11, p. 512, 1914.
[2] Davis and Goucher, Phys. Rev., 10, p. 101, 1917.
[3] Millikan, Phys. Rev., 9, 378, 1917.
[4] Loc. cit., 1917.
[5] K. T. Compton, Phys. Rev., 15, p. 476, 1920.
[6] Van der Bijl, Phys. Rev., 10, p. 546, 1917.
[7] K. T. Compton, loc. cit.
[8] W. Wien, Ann. d. Phys., 60, p. 597, 1919; 66, 1921.
[9] K. T. Compton, Phys. Rev., 16, 282, 1920; Phil. Mag., 40, p. 553, 1920; Phys. Rev., 16, 501, 1920; Phil. Mag., 43, p. 531, 1922; and others in print.
[10] T. C. Hebb, Phys. Rev., 16, p. 375, 1920.

from the incandescent source. It is true that McLennan[1] did attribute the production of "faint arcs" below the minimum ionizing potential to the presence of abnormally high velocity electrons, but only when combined with the effect of absorbed radiation and direct impact does this give a satisfactory explanation.

If radiation plays such an important part in the production of ionization, as has been shown by the works of Professor Compton and his students[2] and of Horton and Miss Davies,[3] it is natural to assume that the conditions which are favorable for the excitation of radiation may also be favorable for the production of ionization. Now the necessary condition for fluorescence of mercury vapor has recently been shown by J. S. Van der Lingen and R. W. Wood[4] to be distillation; mercury vapor in static equilibrium with the metal, or when no liquid is present, does not exhibit fluorescence at any density or temperature. The persistence of fluorescence of mercury vapor in its active or freshly distilled state was observed early in 1914 by Philips,[5] and the time interval between absorption and emission of light in fluorescence has now been measured by Professor Wood.[6] Philips recorded that when the vapor in its stagnant state was excited by the line λ 2536 the resonance radiation extended the width of the tube containing it. But as soon as distillation took place, the radiation became concentrated at the point where the exciting beam entered. A stream of green fluorescent light, originating from the concentrated patch of resonance radiation, passed round the tube with the distilling mercury vapor.

Since the radiation λ 2536 is strongly absorbed by mercury vapor in vacuo at room temperature,[7] it seems that it does not depend on distillation. But that is not entirely convincing, for whenever the vapor is in contact with the fluid metal condensation and evaporation always take place. Perhaps we have this difference: While the few active entities present even in the quiescent state would suffice to produce resonance radiation of a detectable intensity, the number of such entities must be enormously increased in order to exhibit fluorescence. And this has been shown by the work of Van der Lingen and R. W. Wood,[8] who have recorded that with freshly distilled vapor, excited by the short wave-length spark line, the intensity of the emission line λ 2536 is increased to sixty-fold its intensity in stagnant vapor.

[1] McLennan, Proc. Lond. Phys. Soc., 31, 1, 1918.
[2] Loc. cit.
[3] Horton and Davies, Phil. Mag., 41, p. 746, 1921.
[4] J. S. Van der Lingen and R. W. Wood, Astro. Phys. Jour., 54, p. 149, 1921.
[5] F. S. Philips, Proc. Roy. Soc. *A*, 89, p. 39, 1914.
[6] R. W. Wood, Proc. Roy. Soc. *A*, 99, 1921.
[7] R. W. Wood, Phil. Mag., 18, p. 240, 1909.
[8] Loc. cit.

In view of these facts and of the fundamental relation between radiation and ionization, it was thought that valuable information might be obtained if the low voltage arc phenomena were studied under identical conditions for the two cases: (1) When the vapor was very near the liquid surface, and (2) when it was far removed from it. The results are embodied in Part II. of this paper, Part I. being devoted to the study of the effect of the distribution of initial velocities of electrons.

Part I. Effect of Initial Emission Velocities of Electrons on Minimum Ionizing Potentials.

Theoretical Considerations.

In their derivation of the current voltage relation for thermionic currents from a hot cathode, both Child[1] and Langmuir[2] neglected the initial emission velocities of electrons. Richardson and Bazzoni[3] worked out the expression for currents in a gas with elastic electron impacts, and Professor Compton[4] has recently extended it for inelastic impacts. In all these cases the current is proportional to the 3/2 power of the voltage; they differ only in numerical constants and in the part which the mean free path of electrons plays. While the exact relation between current and voltage which takes account of the initial emission velocities requires further investigation,[5] we can see in a general way how it will affect the striking and maintaining voltages in the low voltage arcs.

The effect of space charge is, as we know, to limit the emission of electrons from the incandescent cathode and to change the uniform distribution of potential between cathode and anode. By applying Poisson's equation and on the assumption that the potential gradient is zero at the cathode, a solution is effected. But the emission of electrons with an initial velocity enables some of them to escape in spite of a negative potential gradient near the cathode, so that the surface of minimum potential and zero potential gradient is not at the cathode but a short distance from it. We shall assume that this minimum potential $\overline{V}$ measures the average initial energy of electron emission characteristic of the filament temperature. Accordingly, if V_0 is the true minimum striking voltage, by which we mean the difference between the ionization potential and the radiation potential (so that the sum of the energy absorbed from the radiation and that acquired from the impact may

[1] C. D. Child, Phys. Rev., 32, p. 492, 1911.
[2] I. Langmuir, Phys. Rev., 2, p. 450, 1913.
[3] O. W. Richardson and C. B. Bazzoni, Phil. Mag., 32, p. 426, 1916.
[4] Not yet published.
[5] See paper by W. Schottky, Phys. Zeit., 15, 1914.

equal the energy required for ionization), and if V is the applied striking voltage, we have $V_0 - \overline{V} = V$. In the case of mercury V_0 is given by $V_i - V_r = 10.4 - 4.9$, or 5.5 volts. The observed striking voltage should be $V = 5.5 - \overline{V}$, where $\overline{V}$ depends on the temperature of the filament.

After the arc has struck, the condition changes in two essential aspects. In the first place, the presence of positive ions neutralizes the negative space charge and creates a positive space charge and thus greatly increases the electronic emission by enabling the saturation current to be approached or reached. In the second place the accumulation of positive ions near the cathode creates a "cathode fall," and facilitates the accumulation and ionization of molecules which are in an abnormal state due to absorption of radiation. As a consequence of the increase of total emission, the number of electrons having high velocities must be proportionally increased, although the mean kinetic energy characteristic of the cathode temperature remains the same.

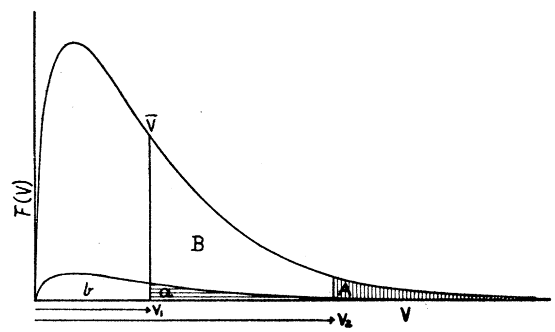


Fig. 1.

Let b = total number of electrons emitted per second just before the striking of the arc; a = the number of those electrons having speed $\geqq$ minimum speed for ionization equivalent to V_0, *i.e.*, the number of effective electrons required to cause the arc; B = total number of electrons after the striking of arc; A = the number of these electrons having speed $\geqq$ minimum speed for ionization equivalent to V_0, *i.e.*, the number of electrons required to maintain the arc.

Then, if V_1 is the initial velocity of electrons expressed in equivalent volts which, combined with the applied voltage V, would make up the required minimum potential for ionization V_0,

$$a = b\int_{V_1}^{\infty} F(V)dV = 2\pi b\left(\frac{e}{\pi kT}\right)^{3/2}\int_{V_1}^{\infty}\sqrt{V}\,\epsilon^{-\frac{eV}{kT}}dV \qquad (1)$$

and a similar expression holds for A, with the integration limit V_2.

On the assumption that it takes the same number of effective electrons to maintain the arc as to cause it, we have $A = a$.

Let F = fraction A/B; $V_1 = \overline{V}$, whence $a/b = 0.39$, as given by the Kinetic Theory.

Then

$$F = 0.39\frac{b}{B}, \tag{2}$$

i.e., 0.39 times the ratio of striking to maintaining currents.

From F and $\overline{V}$, V_2 may be calculated by equation (1). Table I. gives solutions of equation (1) in a form for easy use. The mean energies $\overline{V}$ are twice those characteristic of gas molecules at the same temperature, in accord with the recent work of Sih Ling Ting.[1]

The results may be summarized as follows:

$$\begin{cases} V_0 - V = \text{striking voltage}, \\ V_0 - V_2 = \text{maintaining voltage}. \end{cases} \tag{3}$$

TABLE I.

Filament Current (Amps.).	Temp. K.	$\overline{V}$.	$V_2/\overline{V}$.	F.
15	2100	0.53	1.0	0.392
16	2270	0.57	1.5	0.217
17	2490	0.63	2.0	0.112
18	2620	0.66	2.5	0.062
19	2840	0.75	3.0	0.032
20	2970	0.80	3.5	0.0175
21	3150	0.83	4.0	0.0086
22	3270	0.88	5.0	0.0019
23	3470	0.90	6.0	0.00042
24	3570		7.0	0.00011
			8.0	0.000027
			9.0	0.0000060
			10.0	0.0000014

The first two columns give the temperature of the filament cathode used in the following tests for various heating currents. The temperatures were estimated from the resistances, the small corrections due to the heavy leads being allowed for. F is the fraction of the electrons emitted with energies equal to or greater than $V_2/\overline{V}$ times the mean energy $\overline{V}$.

APPARATUS.

The apparatus for obtaining the arc is shown in the accompanying diagram. Its novel feature was that the liquid mercury itself formed the anode and the distance between it and the coiled tungsten filament was only about 5 mm. The bulb was made of G702P glass and connec-

[1] Sih Ling Ting, Roy. Soc. Proc., A 98, p. 374, 1921.

tion to a mercury diffusion pump was made by a side tube through a mercury cut-off. Before readings were taken, the liquid mercury was thoroughly boiled while the pump was kept in operation. Then the whole bulb and a part of the neck were immersed in a paraffin oil bath of large capacity, thus insuring the regulation of temperature and the supply of fresh mercury vapor. When a good vacuum was attained, as indicated by a McLeod gauge, the filament current was turned on and kept long enough to drive off any gases that might come out from it. Observations were made only at the best possible vacuum.

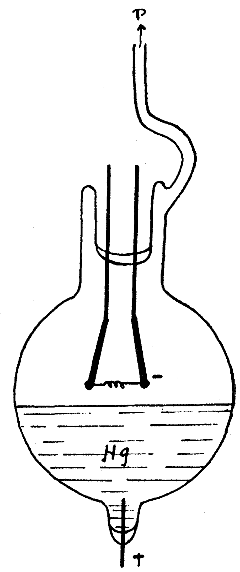


Fig. 2.

The accelerating field was regulated by series and parallel resistances and applied between the anode and the negative end of the filament, so that the voltmeter gave the largest voltage across the arc. The voltmeter reading, less half the voltage drop across the filament, gave the voltage drop between the anode and the middle of the filament. The filament was very short and coiled with three close turns in the middle. These coils, together with the conduction of heat away by the leads, made the central part of the filament much hotter than the rest, so that it behaved somewhat like an equipotential source. At very high temperatures, however, enough electrons may leave near the negative end of the filament to produce the arc. Thus the effective applied voltage should be counted to the middle of the filament at low temperatures, but to some point between the middle and the negative end at higher temperatures. The ionization current was measured by a microammeter with a series of shunts to accommodate it to currents of different sizes.

Results.

Preliminary experiments made at various vapor pressures indicated that the best temperature range for the striking of the arc at low voltages was 130° –150° C. although the actual vapor pressures must be somewhat higher than those indicated by the corresponding temperatures, since the hot filament was so close to the liquid surface. The following results were obtained within this temperature range.

Fig. 3 shows the relation between the current through the filament and the arcing voltage. (2) and (4) were plotted from experimental values of the striking voltages measured to the negative end and the middle of the filament respectively. The correct value must be somewhere between these two limits, near the lower limit at lower temperatures and the upper limit at higher temperatures of the filament. The horizontal line (1) which cuts the ordinate at 5.5 volts indicates the

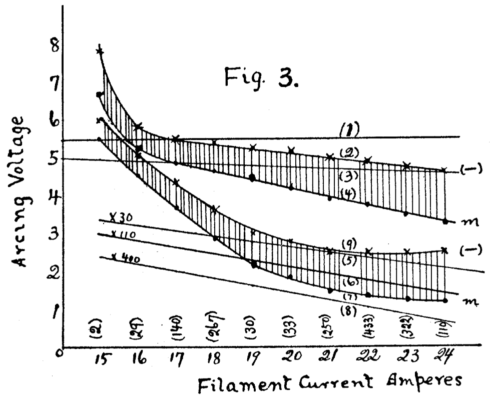


Fig. 3.

theoretical minimum ionization potential, if the electrons were all emitted with zero initial velocity. Curve (3) was obtained from (1) by subtracting the corresponding average initial energy characteristic of each temperature, according to equation (2) and Table I. It lies well within the limits of the experimental curves (2) and (4). The striking voltages at very small filament currents are abnormally high because the total bombarding electron current produces insufficient ionization to cause an arc except at velocities well above the critical minimum velocity.

The nature of the experimental curve is interesting in that it shows strikingly the point of transition characteristic of 4.9 volts. *The fact that the departure from a linear relation between the filament current and the arcing voltage sets in just at the point where the curve crosses the line of minimum ionization potential 5.5 volts in the descending order of abscissæ, is a convincing proof of the fundamental importance of the critical point of 4.9 volts.* Our results have, therefore, confirmed Hebb's findings and removed his objections.

In the case of maintaining the arc, the situation was not so simple. (9) and (7) were experimental curves, while (5), (6), and (8) were obtained from theoretical considerations developed in equations (2) and (3). The ratio of maintaining to striking currents at a particular striking voltage and for a given filament current was found experimentally to range from 30 to 400 as indicated by the numbers in brackets. Substituting any value within this range in equation (2), we get the fraction

F of electrons having initial energy $\geqq V_2$. From Table I., V_2 can be estimated. The theoretical maintaining voltage was then obtained by taking the difference between the theoretical minimum ionizing potential 5.5 volts and V_2 according to equation (3). Curves (5), (6), and (8) show the maintaining voltages calculated thus for assumed current increases of 30, 110 and 400 fold above the pre-arc current. Since the pre-arc current is observed near a point of instability, the observed ratios of current increase are not very accurate, but fall within this range, as shown by the numbers in brackets. With a hot filament, the supply of electrons is adequate, and it is seen that the observed low maintaining voltages agree with those predicted from considerations of velocity distribution as well as can be expected.

A study of the relation between the voltage across the arc and the current through it reveals a very interesting feature. If, after the arc has struck, the series resistance is decreased, the potential across the arc decreases, while the current increases. Beyond the lowest maintaining voltage it begins to rise again with continually increasing current. On increasing the series resistance and therefore diminishing the applied field, the arc potential decreases to exactly the same lowest maintaining voltage, and then rises again, while the current continually decreases. The arc breaks at precisely the same point as where it strikes. The process is perfectly reversible. This phenomenon of reversibility was also observed by Compton, Lilly, and Olmstead[1] in a certain case of the low voltage arc in helium. In the present case the current-voltage changes are always reversible provided the filament is hot enough to cause the arc to strike at a voltage $5.5 - \overline{V}$, although the change immediately following the striking or preceding the breaking of the arc is discontinuous except at very high filament temperatures. If the filament is too cool to permit an arc at a voltage $5.5 - \overline{V}$ (as at 15 amperes in Fig. 3), the arc strikes at a higher voltage but may break at $5.5 - \overline{V}$ volts, and is therefore not reversible in this case.

Fig. 4 is an example among a large number of sets of observations made at various filament temperatures. Curves (1) and (2) show experimental maintaining voltages and currents, the voltages being taken to the negative end and middle of the filament, respectively. The shaded area, therefore, sets the experimental limits within which the true value should lie. The curve (3) was obtained as before from consideration of the initial energy and the increase of electronic emission after the arc struck. Again the agreement is within the probable limits of error. That the theoretical curve departs widely from the experimental curve

[1] Compton, Lilly, Olmstead, PHYS. REV., 16, p. 282, 1920.

after the point of the lowest maintaining voltage is reached is explained by the fact that it is based upon the assumption of an unlimited supply of electrons, whereas, in the actual case, a state of saturation is approached at the lowest maintaining voltage, and, therefore, a higher potential must be applied in order that more electrons may get across the arc.

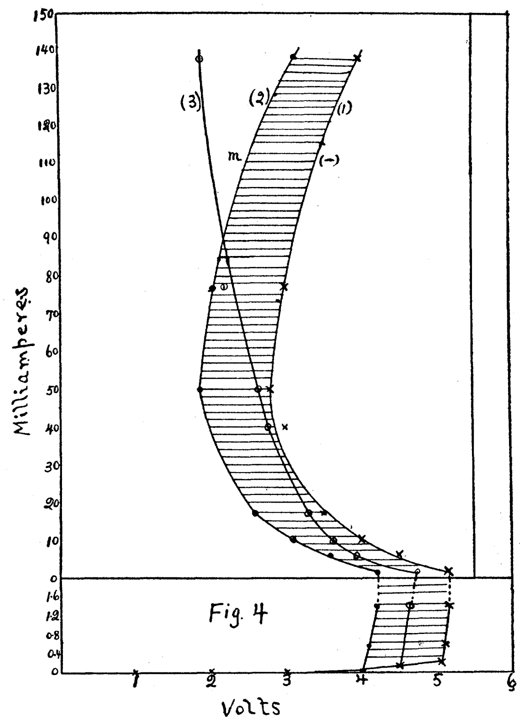


Fig. 4.

Some observations were made in a rapid stream of freshly distilled mercury vapor, close to the liquid surface, and Fig. 5 shows the current-voltage relation. Here we had two distinct breaks, one at 5.5 volts and another at 8.0 volts. The second break was evidently due to the setting in of ionization by single 10.4 volt impacts, the difference between 10.4 and 8 being just about that expected as a result of initial velocity distribution since the maintaining voltage, above the first break, was a little more than 2 volts below the theoretical 5.5 volts. On the return curve it is seen that, in addition to a break at 8 volts, the second arc is maintained to 6 volts. Consideration of relations such as curve (3), Fig. 4, shows that this second arc can reasonably be ascribed to single 10.4 volt impacts. The secondary 8 volt break was not observed with hotter filaments or higher vapor pressures. This is perhaps due to a dearth of normal, unexcited mercury molecules in the immediate neighborhood of the filament when the arc current is very intense. We intend to investigate this point more fully.

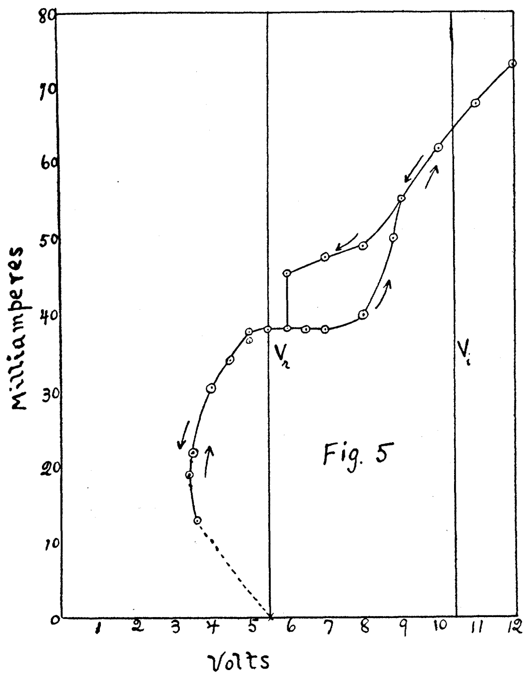


Fig. 5.

Attention may now be called to the fact that the theory developed in this paper can be applied to all gases and metallic vapors. For example, the difference between the ionizing potential and the radiation potential of sodium vapor is $5.13 - 2.1 = 3.0$, but Wood and Okano[1] observed that an arc could be made to strike at .5 volt, leaving 2.5 volts to be accounted for by the initial energy of emission. Compton, Lilly and Olmstead[2] found that the arc could strike in helium at 18.5 volts, while its radiation potential is 20.4 volts; an additional energy of 2 volts must, therefore, come from the initial velocities. In the case of mercury vapor Hebb[3] maintained an arc at 3.2 volts and we have maintained it at 1.8 volts, requiring on the average 3 volts to make up the minimum potential for cumulative ionization. In all three cases tungsten filaments were used, and the fact that the differences are of the same order of magnitude shows that they are characteristic of tungsten rather than that

[1] Wood and Okano, Phil. Mag., 34, p. 177, 1917.
[2] Loc. cit.
[3] Loc. cit.

of the gases used. Where platinum filaments have been used, the arcs have not been obtained at voltages much below the theoretical value. This is to be expected since platinum cannot be heated so hot nor can such a copious electron emission be obtained.

Part II. Effect of Liquid Surface on Arcing Voltage.

First Apparatus.

Having studied the phenomena with liquid mercury very close to the cathode, we proceeded to investigate them with the metal at various distances from it. The apparatus in its first form consisted of a straight tungsten filament (20 mil) with a coaxial cylindrical nickel anode, enclosed in a bulb made of G702P glass. There was a reservoir filled with mercury at a distance of 7 cm. from the cathode. To the main bulb was connected a coil of several turns of small glass tubing 180 cm. in length and 5 mm. in diameter. At the end of this long coil was provided a second reservoir with the mercury surface standing beside and at the same height as that in the first. Thence connection was made to the diffusion pump. The whole was heated by two electric heaters with the heating currents so adjusted as to keep the parts which contained no liquid mercury always at a temperature about 100 degrees higher than that of the reservoirs, the reason being to prevent any condensation from taking place in these regions.

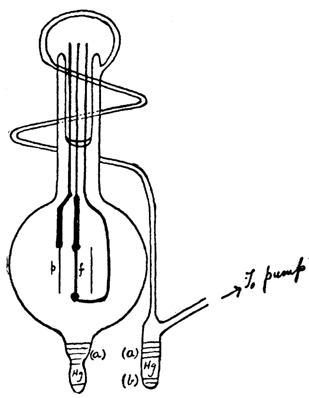


Fig. 6.

The electric connections and the necessary precautions preceding the experiments have been fully described in Part I. The procedure consisted in making observations with liquid mercury in both reservoirs, and then, other conditions being identical, repeating them with no liquid mercury in the main bulb. Owing, however, to the fact that we used large filament currents (from 28 to 34 amperes) with somewhat inadequate leads, and a long pumping system, it was very difficult to maintain a good vacuum for the length of time sufficient to enable us to take a continuous set of readings without impairing the filament. Accordingly, we set the applied voltage at a definite value and observed the striking of the arc by the indication of a sudden jump of the micro-ammeter needle when the filament current was turned on. After one reading had been taken, the filament current was turned off to enable any impurities (which were probably traces of water vapor from the glass near the leads) to be carried away by the pump. When the vacuum again became good, observation was made at some other definite applied voltage; and so forth. By adjusting the accelerating field by very small steps, we were able to determine the lowest striking voltage for a given vapor pressure and filament temperature under fairly good vacuum conditions.

Results with First Apparatus.

Table II. shows the results obtained with this apparatus. The values given in (*a*) and (*b*) under the heading "striking voltage" were averages

Table II.

Temperature of Reservoirs 0° C.	Vapor Pressure in mm.	Striking Voltage (Mean) Measured to the Middle of Filament.		Difference between (*a*) and (*b*) (Volts).
		(*a*).	(*b*).	
110	.48	5.59	6.65	1.06
112	.53	5.25	6.25	1.00
115	.62	5.20	6.95	1.75
119	.76	——	6.90	
120	.80	——	6.52	
121	.82	——	6.45	
122	.87	——	6.85	
123	.91	5.05	6.35	1.20
125	1.00	——	6.86	
127	1.09	5.37	6.50	1.13
129	1.14	——	6.55	
130	1.24	5.15	6.70	1.55
135	1.54	——	6.40	
137	1.67	5.175	——	
138	1.74	5.20	6.30	1.10
145	2.32	5.40	6.30	0.90
			Mean	1.21

(*a*) Distance between the liquid mercury and the cathode = 7 cm.; Filament current: 28–30 amperes.

(*b*) Distance between the liquid mercury and the cathode = 180 cm.; Filament current: 30–34 amperes.

of four or five readings for each temperature. Thus, out of more than 60 readings with vapor pressures ranging from .48 to 2.32 mm., we found no single instance of the effect of 4.9 volts in the case (*b*), which differed from (*a*) only in the distance between the liquid mercury and the cathode. In case (*b*) it was found impossible to produce the arc at low voltages without using a somewhat hotter filament than in case (*a*), as indicated below the table. This change favors the production of the low voltage arc, so that we may say that the 4.9 volt arc did not occur in case (*b*) in spite of more favorable conditions as regards filament temperature. The values in both cases represent definite minimum arcing voltages which could not be diminished by further increase in the filament temperature except by the relatively small amount due to increased initial velocity of emission. It is true that the values of minimum striking voltage in (*a*) and (*b*) do not represent the true values; they merely set the lower limits beyond which the true values cannot go. For the true values are obtained by adding to these values the mean initial energy and a small fraction of half the potential drop in the filament, depending on the point of the filament to which the arc strikes. These corrections are, however, small in comparison with the difference between the values in the two cases, and are approximately the same for both cases. Thus the difference between the two cases is a real one, and is significant.

The mean difference between the two cases (1.21 volts) is almost exactly equal to the difference ($6.7 - 5.5 = 1.2$ volts) which we would expect if the 4.9 volt effect, due to λ 2536 resonance radiation, determines the minimum arcing voltage in mercury vapor near the liquid surface while the 6.7 volt effect, due to λ 1849 resonance radiation, determines the arcing voltage in vapor far removed from the liquid. In any case, we are led to believe that the arcs in these two cases are produced by mercury molecules which are in different conditions.

Second Apparatus.

With a view to confirming the preceding results and throwing some new light upon the problem, the following apparatus was adopted.

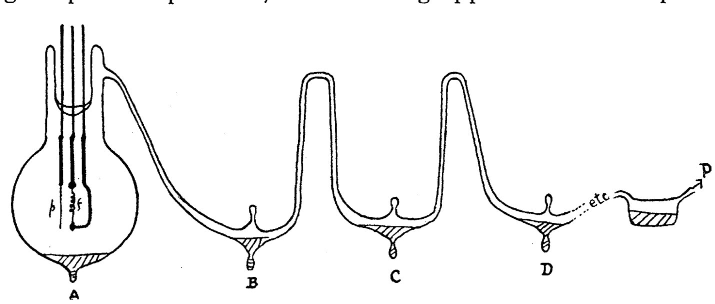


Fig. 7.

Distance of filament f from reservoir: $A = 5$ cm., $B = 35$ cm., $C = 70$ cm., $D = 107$ cm.

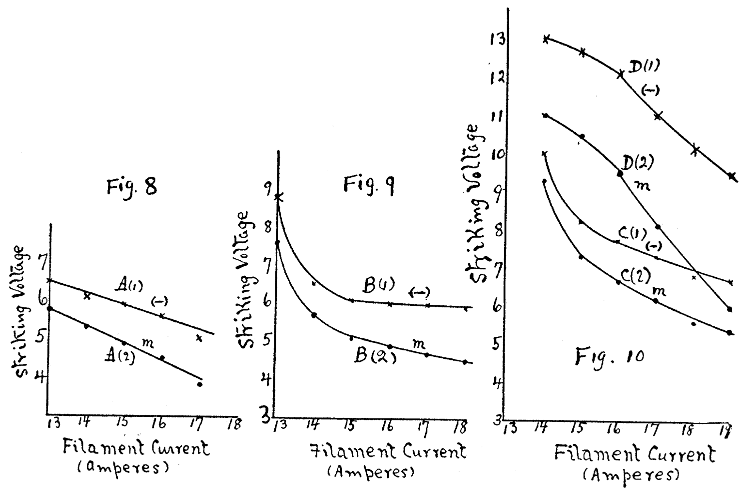
A coiled tungsten filament of five turns with a nickel anode plate was enclosed in the main bulb A, whence connection to the pump was made through a small glass tube of 310 cm. in length. In its course at intervals specified below the diagram, were provided small reservoirs of such design as to make easy the process of filling in and drawing out the liquid mercury. The one nearest the pump was the largest among them. Before the whole was immersed in a paraffin oil bath, the mercury in all the reservoirs was thoroughly boiled. When the whole apparatus was immersed in the hot paraffin oil, to secure the desired vapor pressure, an attempt was made to arrange the heating burners so as to produce a slight temperature gradient to prevent the condensation of mercury in any part of the system nearer to the electrodes than the nearest reservoir containing mercury. This was successful in every case except Case *B*, described below. The procedure consisted in taking in turn readings with mercury in the reservoirs *A*, *B*, *C*, and *D*; *B*, *C*, and *D*; etc. Great care was taken to clean mercury from the path leading from the electrodes to the nearest filled reservoir, while keeping the succeeding reservoirs full of mercury. The reason for keeping succeeding reservoirs full was to prevent any rapid stream of mercury vapor from passing over from the experimental reservoir, thus insuring approximately an equilibrium condition and a vapor pressure really characteristic of the temperature. The difficulty mentioned above, of getting a good vacuum after the filament current was turned on, was minimized by using a tungsten filament of lesser size and with larger leads.

Results with Second Apparatus.

Since we had found the effect of the liquid surface within a wide range of vapor pressures, we confined ourselves now to the study of the relation between the filament current and the striking voltage at some suitable vapor pressures. The results were as follows.

Case A.—The distance between the liquid mercury in the reservoir *A* and the cathode was 5 cm. Here no trace of the effect of 6.7 volts was found; all effects were due to that of 4.9 volts. The relation between the filament current and the striking voltage was linear, in conformity with our previous results in Part I. See Fig. 8. *A*(1) is measured to the negative end and *A*(2) to the middle of the filament. The difference between the observed voltages and 5.5 volts is accounted for by initial velocity of emission, as shown in Part I.

Case B.—The distance between the liquid mercury in the reservoir *B* and the cathode was 35 cm. Here the values of the striking voltage at higher filament temperatures were only slightly higher than those in Case *A*. The 4.9 volt arc was still prominent. After the readings had been taken, it was found, however, that a trace of liquid mercury had been left by mistake in the reservoir *A* and condensation had taken place along the tube leading from the reservoir B to the cathode, indicating that there had been a stream of mercury vapor in toward the electrodes. The significance of this case will be discussed later. See Fig. 9.



Figs. 8, 9, 10.

Case C.—The distance was increased to 70 cm. If we compare the curves $C(1)$ and $C(2)$ in Fig. 10 with $A(1)$ and $A(2)$ in Fig. 8, we see that there was on the average a difference of 2.0 volts in the values of the striking voltage. Since in Case A we have positively identified the effect of 4.9 volts, the production of arcs in Case C must be due to that of a higher critical voltage, presumably 6.7 volts.

Case D.—A new tube leading from the main bulb to the reservoir D was used, with a distance between the liquid mercury and the cathode equal to 107 cm. The position of the main bulb was so tilted that no liquid mercury could possibly enter or stay in it. At the end of Case C, the filament was burned out and a new one was put in. Unfortunately, it was a little too long, and in consequence the potential drop across it was rather large, which rendered the true values of the striking voltage a little uncertain. But even in this case the experimental curves did set the limits within which the true value at the highest temperature should lie. The vacuum conditions in this case were particularly satisfactory. See Curves $D(1)$ and $D(2)$ in Fig. 10.

In all these cases it has been brought out unmistakably that the striking voltages, corrected for initial energy of electrons, all tend toward definite minimum values as the highest filament temperature was approached. This is especially evident when it is remembered that the arcing voltage, corrected for filament drop, lies between curves (1) and (2), Fig. 3, in all these cases, and is nearer curve (2) at lower temperatures and curve (1) at the highest temperatures. When the liquid mercury was very near the cathode, the limiting value was in the neighborhood of 5 volts. When it was far removed, this was never below 6 volts. Another very noticeable fact, which strengthens the belief that we are really dealing with two different types of arc, is that, when near the liquid surface, the arc not only struck at a lower voltage but would strike much more easily, *i.e.*, with lower filament temperatures and much less care regarding good vacuum conditions, than when the liquid surface was remote.

The contrast between these two cases finds its expression also in the curves in Figs. 11 and 12. The changes between the striking and breaking voltages were reversible in both cases; but in one the arc struck and broke at 6.2 volts with less filament current and in the other at 7.5 volts with larger filament current. Voltages are given to the negative end of the filament in both cases.

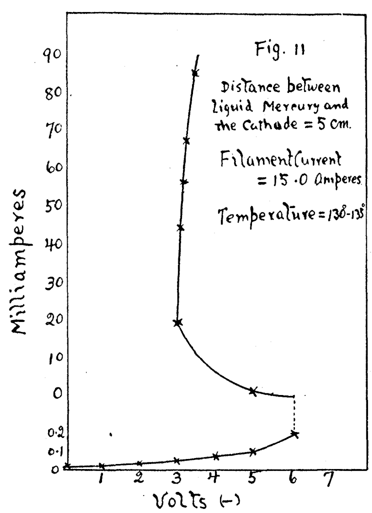


Fig. 11.

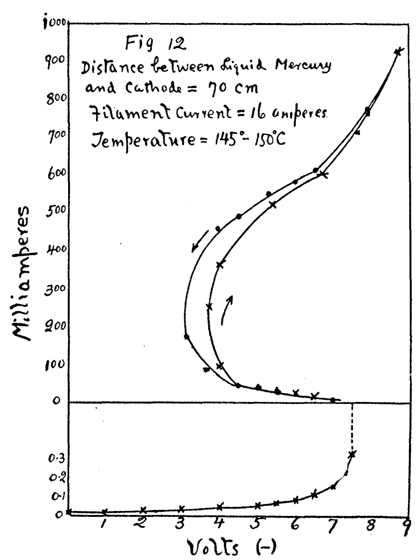


Fig. 12.

Third Apparatus.

If there is still any doubt about the existence of two types of arc, the following experiments will help to remove it. The apparatus was designed to permit the attainment of the highest possible purity of mercury vapor and greater flexibility in methods of testing. The first end was attained by constructing the apparatus so that it formed of itself a diffusion pumping system in which any impurities evolved in the region of the electrodes were automatically carried away toward the vacuum pump by the motion of the mercury vapor. This is evident from the construction shown in Fig. 13.

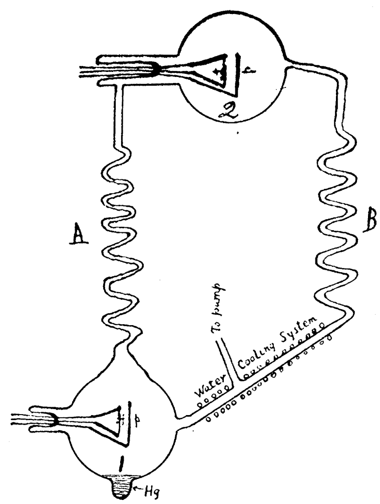


Fig. 13.

Two bulbs with identical electrodes were connected by two equal pieces of glass tubing, so as to form a closed circuit. A water cooling jacket was provided near the connection to the pump, as shown. The whole was enclosed in an electrically heated asbestos oven so arranged as to maintain a small upward temperature gradient, thus preventing any condensation of mercury in the tubes *A* or *B* or in bulb (2). Before making observations the mercury was thoroughly boiled, the glass parts well baked out and the electrodes thoroughly glowed, a high vacuum being maintained by a two-stage diffusion pump.

Observations of the striking and maintaining voltages of the arc were made with various filament currents in the following four conditions: (*a*) in bulb (1) in stagnant vapor (with the water-cooling system not in operation); (*b*) in bulb (2) in stagnant vapor; (*c*) in bulb (1) in moving vapor (with the water-cooling system in operation); (*d*) in bulb (2) in moving vapor. In cases (*a*) and (*b*) the vapor pressure was the same. In case (*d*) the vapor pressure would be about half that in case (*c*) owing to the fall in pressure along the tube of moving vapor. This was compensated very nearly by using a slightly higher temperature of the mercury reservoir in case (*d*) than in case (*c*). Thus any difference between the results in cases (*c*) and (*d*) cannot be attributed to difference in vapor pressure, since the earlier experiments showed that the striking voltage was practically constant over a considerable range of pressures. These four cases were tried with tubes *A* and *B* of 100 cm. length and 5 mm. diameter, and again with tubes of 50 cm. length and 1 cm. diameter. Experiments were tried at various temperatures of the mercury reservoir between 130° and 150° C.

Results with Third Apparatus.

The results entirely confirmed those with the first two types of apparatus. Table III. is an example, taken with tubes *A* and *B* of 100 cm. length and stagnant vapor, cases (1) and (2).

TABLE III.

Filament Current (Amperes).	Striking Voltage to Negative End of Filament.		Difference between (*a*) and (*b*) (Volts).	Maintaining Voltage to Negative End of Filament.		Difference between (*a*) and (*b*).
	(*a*).	(*b*).		(*a*).	(*b*).	
13.........	7.2	8.55	1.35	5.1	5.8	0.7
14.........	6.7	7.90	1.20	3.8	4.3	0.5
15.........	6.1	7.77	1.67	3.2	3.85	0.75
16.........	5.9	7.20	1.30	3.1	3.67	0.57
17.........	5.7	7.00	1.30	3.0	3.57	0.57
18.........	5.5	6.70	1.20	3.0	3.3	0.30
			Mean = 1.33			Mean = 0.56

The average difference between the striking voltages in the two cases was 1.33 volts, agreeing well with the suggested theoretical difference of 1.2 volts. The difference between the maintaining voltages was less, and is probably not significant.

Results practically identical with those above were obtained in the moving vapor in tubes *A* and *B* of 100 cm. length and in stagnant vapor with tubes of 50 cm. length. In moving vapor with tubes of 50 cm. length a small liquid surface effect was shown in the current-voltage curve of bulb (2). This suggests that the apparatus may be modified to permit measurement of the life period of the abnormal mercury molecules which originate at the surface of evaporation. Such an investigation can not be included in the present paper.

DISCUSSION.

The question arises as to whether the difference between the values of the striking voltage in these two cases may not be attributed to impurities. For, one argues, if mercury vapor diffuses from the bulb containing the electrodes, this vapor will carry out any impurities which may be given off in the bulb, and thus create a better vacuum in case the liquid is placed under and very near the cathode. On the other hand, if the liquid is far away, these foreign gases would hinder the production of a good vacuum in the arcing space, and, therefore, a higher potential would be required in order to produce the arc. We have direct experimental evidence to show that this objection is unfounded. In the first place, the distribution of mercury reservoirs was such as to preclude any considerable motion of mercury vapor in the first two types of apparatus, as previously pointed out. In the second place, we found by experience that, with mercury very close to the cathode, it was exceedingly easy to get the 4.9 volt arcs at low voltages, even when the vacuum was not very good. But, if the liquid surface was far away, a slightest trace of impurities rendered the production of the 6.7 volt arc difficult, and the 4.9 volt arc was never obtained. In the third place, we have the Case *B* with the second apparatus where the indication was such as to show that the direction of the stream of mercury vapor was from the distant reservoir *into* the arcing space, and if there were any impurities they must drift along that direction and tend to be retained in the bulb. Yet the 4.9 volt arc appeared just the same. This fact alone suffices to remove the objection quite apart from the numerical agreement with the theoretical values. Finally, in the third apparatus, conditions for removal of impurities were ideal.

Another suggested criticism is that, if we were working with mercury molecules in an abnormal state, the liquid surface ought to have no influence as soon as *equilibrium* has been established. But it must be remembered that the molecule of a freshly distilled vapor remains in its abnormal state only for a short interval, during which it is more capable of absorption of radiation, which in turn renders it easily ionized by direct electronic impacts. This condition is fulfilled when the liquid surface and the filament are very close to each other. If they are far apart, then by the time it reaches the arcing space the molecule has already returned to its normal state, or to a state in which it will not so readily (if at all) absorb the resonance radiation λ 2536; hence a higher potential must be applied, probably high enough to stimulate the λ 1849 radiation. The question whether, or to what relative extent, λ2536 will be absorbed by the vapor in a tube containing no liquid mercury is important, and should be investigated, as has been pointed out by Professor Wood.[1]

Closely related may be the work of McLennan and Shaver,[2] who have found that, by the photographic method as well as by the use of thalofide cells, non-luminous mercury vapor does not absorb radiation of the wave-length λ 10140. But if there are scarcely visible deposits of mercury in the tube it shows marked absorption of this radiation. This may account for the absorption of λ 10140 by non-luminous vapor observed by Dearle.[3] It would be interesting to study the absorption by a long column of mercury vapor with the exciting light parallel to and grazing the liquid surface as compared with the absorption at some distance from the mercury surface, as Professor Compton once suggested.

Whatever may be the interpretation, it is now experimentally proved

[1] Loc. cit.

[2] McLennan and Shaver, Proc. Roy. Soc., 100, p. 200, 1921.

[3] Dearle, Roy. Soc. Proc., *A*, 92, p. 608, 1916; 95, p. 280, 1919.

that there is a close relation between the production of arcs on the one hand and the excitation of fluorescence and resonance radiation on the other, in mercury vapor. These experiments also open the question as to the origin of the spectral lines λ 2536 and λ 1849. According to the Quantum Theory, the resonance potential of 4.9 volts corresponds to the first term of the combination triplet series $1S - mp_2$ and that of 6.7 volts to the first line of the principal singlet series $1S - mP$. And according to the Bohr theory it means that the line λ 2536 is emitted when the electron falls from the $1p_2$ orbit to the $1S$ orbit, and when it falls from $1P$ to $1S$ the line λ 1849 is emitted. In the light of our experiments these lines seem to originate from different entities. The suggestion,[1] that diatomic molecules may come out from a freshly distilled vapor and account for the fluorescence is, apart from lack of chemical evidence, not supported by the positive ray spectrum of mercury, nor is it in accord with Bohr's theory of radiation. These experiments, therefore, suggest more problems than they attempt to solve, and it is to be hoped that further investigation along these lines may throw some light on the problems. For the fact that λ 2536 and λ 1849 belong to series having identical convergence limits and the fact that there is only one ionization potential, 10.4 volts, makes it very unlikely that there are really two different entities. The most plausible explanation in the light of present knowledge seems to be that there is some slight influence either due to arrangement of internal electrons or to influence of neighboring molecules which increases the probability of ionization along the $1S - mp_2$ path as compared with the $1S - mP$ path in freshly distilled vapor, but that this influence does not appreciably affect the potential energy of the electron in the $1S$ state. In other words, the direction or size of the force on the electron may differ while the energy does not. This is, of course, dynamically possible.

In conclusion, I wish to express my sincere thanks to Professor K. T. Compton, who suggested this research and under whose direction it was carried out.

Palmer Physical Laboratory,
Princeton, New Jersey,
August 14, 1922.

[1] J. S. Van der Lingen and R. W. Wood, loc. cit.