POTENTIAL DROP AND IONIZATION AT MERCURY ARC CATHODE

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Abstract

By means of a movable Langmuir collector, the potential, ion concentration and electron temperature were measured at various distances from a stationary mercury cathode spot, at various arc currents. The results indicated a cathode drop of 10.0 volts, and a small negative potential gradient beyond the fall space which was more pronounced at the larger currents. The ion concentration varied between $2(10)^{13}$ and $3(10)^{11}$ cm^{-3} for distances between 0.4 cm and 1.7 cm and arc currents between 11 amp and 4.2 amp. The concentrations evidently greatly exceed these values very close to the cathode. The mean electron energies were about 1.4 volts near the cathode and fell to a little less than a volt at the greater distances. From the lack of saturation of currents to the collector at space potential, the coefficient of electron reflection at the amalgamated tungsten collector surface was found to be close to 0.5. It is shown that the thickness of the cathode fall space must be less than $1.76(10)^{-4}$ cm and that the field at the cathode surface must exceed $7.6(10)^{4}$ volts $\cdot$ cm^{-1}.

Introduction

In 1905, Stark and his collaborators[1] attempted by a probe wire method to measure the cathode fall of potential in a mercury arc, and their value of 5.27 volts has been accepted until quite recently. In 1924, Langmuir and Mott-Smith[2] pointed out a serious error in the old probe wire method, and developed a new method which not only gives accurate values of space potential, but also gives information regarding electron and ion concentrations and velocities. In 1928, Killian, at the suggestion of one of the authors, undertook an investigation of the potential drop and conditions of ionization near mercury arc cathodes. His results were reported at a meeting of the American Physical Society[3] and were essentially as follows: The drop in potential from the cathode to a point distant 0.2 cm from its surface was 10.1 volts, and increased regularly to 11.6 volts as the distance was increased to 3.0 cm. The value of about 10 volts, as extrapolated to the cathode surface has been taken as significant of the ionizing potential of mercury within the limits of uncertainty set by the small unknown contact difference of potential between cathode and probe.[4] Later work by Nottingham[5] has led to similar conclusions

[1] Stark, Retschinsky and Shaposchnikoff, Ann. d. Physik **18,** 213 (1905).

[2] Langmuir and Mott-Smith, G. E. Rev. **27,** 449, 538, 616, 762, 810 (1924).

[3] Killian, Phys. Rev. **31,** 1122 (1928).

[4] Gaudenzi (The Brown Boveri Rev. **16,** 303 (1929)) estimated the cathode drop to be about 9 volts by a method which did not allow for the possibility of a positive or negative anode drop.

[5] Nottingham, J. Frank. Inst. **206,** 43 (1928); **207,** 299 (1929).

in some arcs at higher pressures with various cathode materials. Killian furthermore found random currents of positive ions of 1.5 to 40 milliamps·cm^{-2} and of electrons of 1.3 to 18 amps·cm^{-2}, the larger values referring to the regions closest to the cathode. The electron temperatures were 5000° to 16,500°K, or 0.65 to 2.13 volts mean energy.

In these measurements, the distances were measured from the cathode surface but do not represent true distances from the cathode spot, since it wandered rapidly and erratically all over the cathode surface. Killian there-

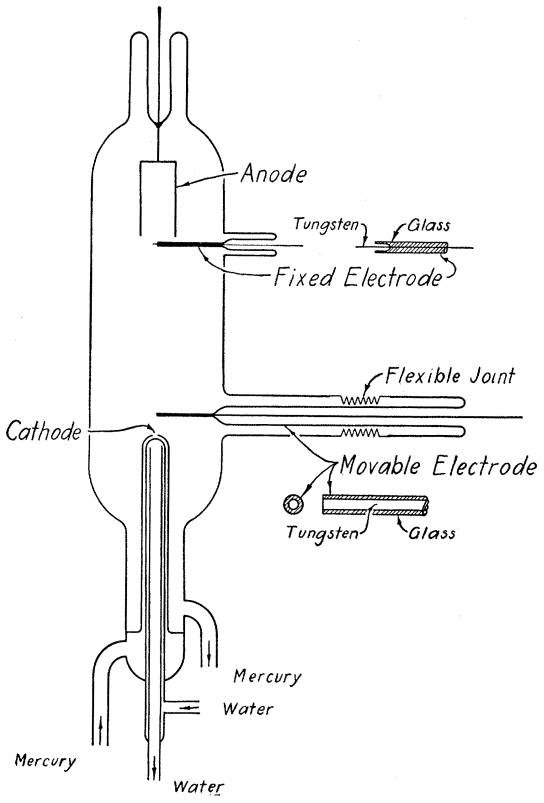

Fig. 1. Diagram of arc tube.

fore devised the apparatus described below in order to keep the cathode spot approximately stationary and thus to make possible more accurate measurements. Since Killian was diverted from carrying out these more refined experiments, the authors continued them as follows.

Apparatus

A diagram of the arc tube is shown in Fig. 1. The cathode consists of three coaxial tubes. The innermost two are of Pyrex glass and constitute a water-cooling system for the cathode. The outside tube is of quartz and has a small hole drilled in its upper end. Mercury is raised to the level of this hole.

The surface of the mercury at the hole is the cathode of the arc. The small size of the pool cathode thus prevents excessive wandering of the cathode spot. The mercury outlet shown is designed to take care of the mercury that condenses on the walls of the tube and falls to the bottom.

The exploring electrode employed in the region of the cathode consists of a 60 mil tungsten wire entirely covered with glass, and then ground flat at its end. The resulting flat tungsten surface constitutes a plane collector, and the great mass of tungsten behind it makes its thermal dissipating power sufficiently great to prevent the excessive heating which has hitherto made measurements very near the cathode spot impossible. The flexible metal joint shown in the diagram permits an exploring range of about 2 cm.

The exploring wire shown near the anode is of the usual type consisting of a fine tungsten wire covered with glass over most of its length. The last few millimeters of glass are not in contact with the exploring wire. This prevents electrical contact between the exploring wire and any metal coating which may be deposited on the insulating glass.

The anode as shown is of the usual hollow cylindrical design and is made of sheet nickel.

PROCEDURE

The arc was started by means of a high frequency leak tester and the current was adjusted to the desired value by varying the resistance in series. The arc and series resistance were operated on 110 volts d.c.

The experimental procedure, after the arc had become steady, was to measure the current to the collector for different voltages applied to it at various distances from the cathode. At any given position, a plot of log i vs. V where i is the electron current to the collector and V the potential of the collector with respect to the cathode generally showed the points to be scattered between two parallel lines a half volt apart. This scattering of the points was found to arise from changes in the nature of the surface of the collector which resulted in changes in the contact difference in potential and depended on the immediately previous history of the collector. It was found that consistent results were obtained if the collector was left 100 volts negative with respect to the anode except when a reading was actually being made. Under these conditions the points fell along a curve at the lower voltage limit mentioned above, indicating a low value for the work function of the surface.

The curves shown are plotted to this lower value, which is believed to be the correct value, for reasons indicated below. Since the collector is always covered with a thin visible film of mercury, there is no further correction necessary for contact difference of potential between collector and mercury cathode.

A typical collector curve is shown in Fig. 2.

INTERPRETATION OF SHIFT IN COLLECTOR POTENTIAL

We were at first inclined to attribute the shift in collector potential, when its potential to space was changed from large negative values to small negative or positive values, to a slow deposit of alkali material coming perhaps

from the neighboring glass and depositing as ions when the collector is negative. In this case the upper curve (characteristic of the collector in its more electronegative state) would presumably be that characteristic of an uncontaminated surface and, if so, the correct values would be 0.5 volt higher than those of Fig. 2. This was our opinion at the time of our preliminary report to the American Physical Society (Washington Meeting April 24, 1930), when we reported as our best estimate that the cathode drop is equal to the minimum ionizing potential 10.4 volts. Now, however, we are inclined to interpret the results differently, and to use the lower value of potential for the following reasons.

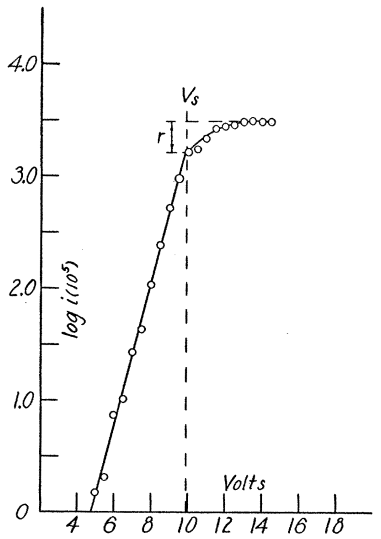

Fig. 2. Curve showing logarithm of electron current i as a function of collector potential V_c with respect to cathode. V_s is space potential and r indicates the amount of electron reflection.

After remaining 100 volts negative for a short time, surface impurities should be sputtered off by positive ion bombardment, leaving a clean collector surface. Hence the measurements made just after this should be those characteristic of the clean surface. Furthermore Found and Langmuir (unpublished) in extending earlier work by Kenty and Turner,[6] found that oxygen layers could form slowly on tungsten collectors even in very pure gas, causing electronegative potential shifts of about 0.5 volts in the surface potential. We think it probable, therefore, that the lower voltage values are the correct ones, indicating the value of the cathode drop to be about 9.9 volts.

Interpretation of Experimental Results

These and similar curves are interpreted by the collector theory of Langmuir and Mott-Smith, which is now too well known to require comment further than to give the equations which we shall use:

[6] Kenty and Turner, Phys. Rev. **32**, 799 (1928).

$$I = I_0\epsilon^{-eV_c/kT},\quad I_0 = Ne\left(\frac{kT}{2\pi m}\right)^{1/2},\quad i = AI$$

where I is the electron current density to the collector whose potential is $-V_c$ with respect to the space, I_o is the random electron current density, N and T are the electron concentration and temperature, respectively, and A is the collector area. From these equations we have:

$$\log i = \log AI_0 - \frac{eV_c}{kT} = \log ANe\left(\frac{kT}{2\pi m}\right)^{1/2} - \frac{eV_c}{kT}$$

which is the equation of the straight portion of the curve of Fig. 2, when V_c is taken to be the value of V measured from the point of discontinuity which is at space potential V_s. The fact that the curve to the left of the discontinuity is straight, proves that the electrons have a Maxwellian distribution of velocities, which is assumed in the above equations.

It is observed that the electron current to the collector does not reach its maximum value at space potential, but only when the collector is a few volts positive with respect to space. This is attributed to electron reflection from the collector, and the intervening curve depends on the distribution of velocities of the reflected electrons. Such reflection, which is a well-recognized phenomenon, does not affect the slope of the straight line to the left of the break, since it is a peculiarity of a Maxwell distribution that it is not altered by a retarding field and hence the fraction of electrons reflected is constant at all values of the retarding field. The effect of reflection on the straight portion of the curve is thus simply to depress it, parallel to itself, by an amount dependent on the reflection coefficient.

This reflection coefficient may be obtained from Fig. 2 as follows. The electron current has reached saturation at about 4 volts above space potential, indicating that practically no reflected electrons can escape against as much as 4 volts. The difference between this saturation current and the current at the discontinuity represents the current of reflected electrons, and is shown by r in Fig. 2. The ratio of this reflected current to the total saturation current gives the reflection coefficient R. Owing to the foreshortening of the logarithmic scale, these values of R are determined with less experimental accuracy than the other quantities in which we are interested.

The more important results of the measurements are shown in Figs. 3 and 4. The mean electron energy $\bar{V}$ was calculated from the relation

$$\frac{e\bar{V}}{300} = \frac{3}{2}kT$$

and represents the mean energy of the electrons in a given volume. For the mean energy of the electrons striking the collector, the fraction 3/2 should be replaced by 2.

The data shown in Figs. 3 and 4 were all obtained with an arc carrying 4.2 amps. Similar observations on an 11.0 amp. arc yielded results which, for comparison, are shown in Table I.

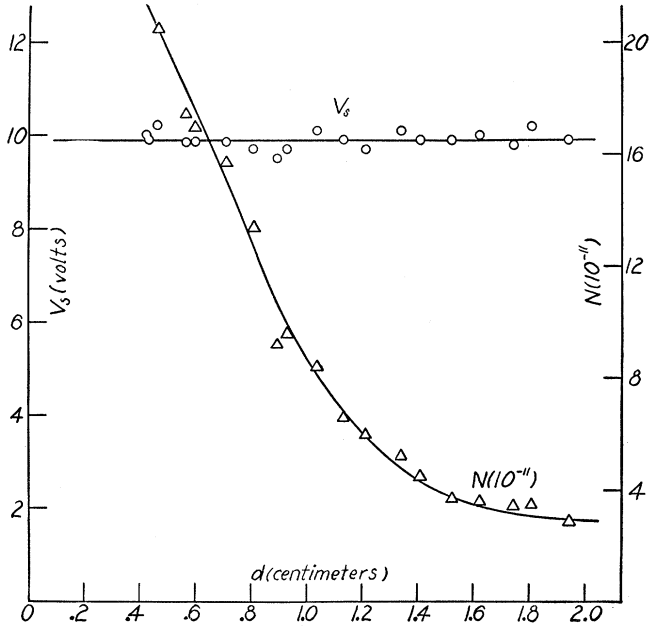

Fig. 3. Space potential V_s with respect to the cathode and electron concentration N as functions of the distance d from the cathode spot to the center of the face of the 60 mil (0.15 cm) diameter collector. Arc current 4.2 amp.

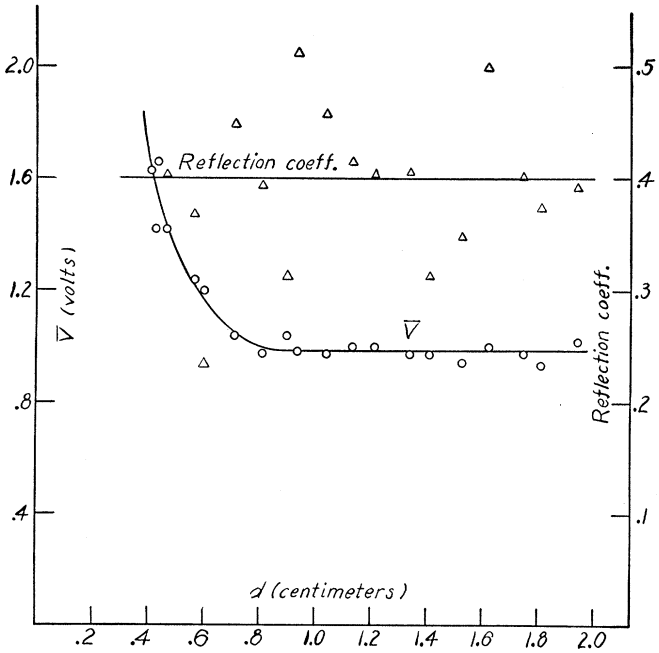

Fig. 4. Mean electron energy $\bar{V}$ in equivalent volts and reflection coefficient R as functions of distance d from cathode spot to collector. Arc current 4.2 amp.

TABLE I. *V_s = space potential; N = electron concentration; $\overline{V}$ = mean electron energy; I = random electron current density; d = distance from cathode.*

	4.2 amp. arc		11.0 amp. arc	
d(cm)	0.43	1.75	0.39	1.71
V_s (volts)	10.0	9.8	10.2	8.9
I (amp·cm^{-2})	5.7	7.4	63.5	12.8
N (10^{-11})	17.1	2.8	218.	55.3
$\overline{V}$ (volts)	1.42	0.978	1.171	0.748

DISCUSSION OF EXPERIMENTAL RESULTS

Cathode drop. From such results we conclude that the cathode drop is very near to 10 volts, from the nearest point at which we can measure (or extrapolate) to the cathode. Of course what we really wish to know is the cathode drop across the cathode fall space alone, which is an extremely small distance. This distance has never been measured, but may be estimated roughly as follows: The relations in the cathode fall space are given by the space-charge equation

$$I_+ = 0.543(10)^{-7}\frac{V_c^{3/2}}{M^{1/2}d_c^2}$$

in ordinary electrical units. The current density at the cathode[7] is about 4000 amp.·cm^{-2}. Langmuir and Mott Smith[8] have shown that a negative electrode immersed in strongly ionized mercury vapor collects a positive ion current of about 1/400 of the "random" electron current, which in turn is always larger than the "drift" (or actual discharge) current. Since the drift current density is 4000 amp.·cm^{-2}, the positive current density is therefore something greater than 1/400 of this, i.e., greater than 10 amp.·cm^{-2}. Unfortunately we cannot say how much greater than this lower limit is the true value of the positive current. Two factors may increase it by considerably more than the factor of three or four which commonly represents the ratio of random to drift current in regions of uniform ionization. One of these is the enormous concentration of electrons and ions in the region of negative glow on account of the potential maximum which develops in this region of intense ionization, and the consequent "trapping" of electrons to build up large concentrations, and the other is the additional trapping action due to the fact that the cathode spot is a depression in the mercury surface and presents therefore the peculiarities of a hollow cathode.

Perhaps the positive ion currents may be ten, though probably not a hundred times the value given by the fraction 1/400.[9] Using this as a lower limit, and taking $V_c = 10$ volts and $M = 200$, we find

$$d_c < 1.76(10)^{-4}\text{ cm}.$$

[7] Güntherschulze, Zeits. f. Physik **11,** 74 (1922).

[8] Langmuir and Mott-Smith, G.E. Rev. **27,** 544 (1924).

[9] From the theory of collectors in ionized gas (Tonks and Langmuir, Phys. Rev. **34,** 876 (1930)) it is impossible that the positive current density at the cathode spot can be less than

Field at cathode. Given a cathode drop of 10 volts in a distance less than $1.76(10)^{-4}$cm, we calculate the average field in the fall space to be greater than $5.7\ (10)^4$ volts$\cdot$cm^{-1}. By the simple space-charge equation it is easily shown that the field E_c at the cathode surface is 4/3 the mean field, or

$$E_c > 7.6(10)^4 \text{ volts}\cdot\text{cm}^{-1}.$$

It appears unlikely that the field can be as much as ten times this value, since this would require an ion current one hundred fold that on which the calculation is based. These results are not appreciably affected if we use the more refined equations of Mackeown[10] to calculate the value of d_c.

Of course the cathode surface is highly agitated and consequently rough. Thus the fields to points may greatly exceed the values calculated above, and may very likely attain values of the order of millions of volts per centimeter. Langmuir[11] has already pointed out that fields of this magnitude are probably adequate to account for the observed electron emission from the cathode spot as "autoelectronic" emission, or "field current".

In the absence of information regarding the behavior of a fresh mercury surface in autoelectronic emission and in view of the uncertainty regarding the field strength at the cathode, it appears hopeless to make a direct quantitative test of this theory of emission from the cathode spot. Further evidence, however, is afforded in a revision of earlier studies of heat balance, as given in the following paper.

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this. According to one theory it might be much greater (the theory of thermal ionization of the vapor by Slepian, Phys. Rev. **27,** 407 (1926)). As shown in the following paper, however, there are not only serious theoretical objections to this theory, but the experimental evidence based on heat balance at the cathode is inconsistent with it, and points to the correctness of the assumption that the relative current densities are at least of the order of those to be expected if the cathode acts toward the positive ions simply as a collecting electrode.

[10] Mackeown, Phys. Rev. **34,** 611 (1929).

[11] Langmuir, G. E. Rev. **26,** 735 (1923).