PHYSICAL REVIEW VOLUME 109, NUMBER 3 FEBRUARY 1, 1958

Emission Mechanism of Cold-Cathode Arcs*

K. G. Hernqvist
Radio Corporation of America, RCA Laboratories, Princeton, New Jersey
(Received August 15, 1957)

A new theory for the electron emission mechanism of cold-cathode arcs is proposed in which excited atoms play a predominant role as a source for ion generation in the vicinity of the cathode surface. The processes of resonance ionization of excited atoms at the cathode surface and of ionization of excited atoms in the strong electric field at the cathode surface are considered.

Special emphasis is given to the dispersed (or *D*-type) arc which operates with a relatively low emission current density. An analysis of the *D* type of arc is given based on the proposed theory. Recent studies of this arc are shown to corroborate the theory.

The rapid decrease of electron plasma temperature and population of excited atoms during arc-current interruption offer an explanation for the short extinguishing time of cold-cathode arcs.

I. PROBLEM OF THE EMISSION MECHANISM OF MERCURY POOL ARCS

STUDIES of the mercury pool arc[1] have indicated that electrons emitted from the cathode come from the top of the Fermi energy distribution in the cathode and not from the top of the potential barrier of the undisturbed mercury surface. The behavior is analogous to that of field emission[2] (tunnel effect) where there is a large electric field at the cathode. There are two important questions to be answered in connection with the field emission mechanism of mercury pool arcs: (1) How is the high electric field necessary for field emission maintained at the cathode surface? (2) Why does the emission cease after arc-current interruptions as short as 10^{-9} to 10^{-8} second?

To answer the first question, the electric field at the cathode surface due to the ion space-charge sheath between the plasma and the cathode is usually considered.[3,4] The electric field E_c in volts/cm is given by the Mackeown relation,

$$E_c^2=7.57\times10^5 V_c^{\frac{1}{2}} j_e\left[\left(\frac{m_p}{m_c}\right)^{\frac{1}{2}}\frac{j_p}{j_e}-1\right], \tag{1}$$

where V_c is the cathode drop in volts, j_e is the electron emission current density in amperes/cm^2, j_p is the ion current density in amperes/cm^2 and m_p/m_e is the ion-to-electron mass ratio. The expression for j_e is given by the Fowler-Nordheim relation[2] for field emission:

$$j_e=6.2\times10^{-6}\frac{E_c^2}{\phi}\exp[-6.8\times10^7(\phi^{\frac{3}{2}}/E_c)], \tag{2}$$

where ϕ is the work function of the cathode. Equations (1) and (2) yield

$$j_e=6.11\times10^9\frac{\phi^3}{V_c^{\frac{1}{2}}\left[\left(\frac{m_p}{m_e}\right)^{\frac{1}{2}}\frac{j_p}{j_e}-1\right]\ln^2\left[4.69\frac{V_c^{\frac{1}{2}}}{\phi}\left(\left(\frac{m_p}{m_e}\right)^{\frac{1}{2}}\frac{j_p}{j_e}-1\right)\right]}. \tag{3}$$

For the mercury pool arc[1,5] $\phi=4.52$ volts, $V_c\approx10$ volts, $(m_p/m_e)^{\frac{1}{2}}\approx600$, and $j_p/j_e\approx1/50$ yielding $j_e\approx1.2\times10^9$ amperes/cm^2. The effects of the image force and field enhancement due to the roughness of the cathode surface have not been taken into account in Eq. (3). These effects may be expected to somewhat lower the requirement on current density. Although current densities in excess of 10^6 amperes/cm^2 have been observed,[6] it is doubtful if they are sufficiently high to satisfy the Mackeown theory. Furthermore, measurements on anchored arcs[7] have yielded lower values for the emission current density. This dilemma was highlighted in 1953 when Smith[8] reported on what was thought to be a special mode of the mercury pool arc, called the dispersed or *D* type of arc, for which the current density may be as low as 10 amperes per square centimeter.

The second question relates to the extremely short extinguishing time[9,10] of mercury pool arcs. If a short negative pulse is applied to the anode of a running dc arc such as to cut off the anode current during times as short as 10^{-9} second, the arc will not refire when the anode voltage is brought back to a high value. Plasma density decay is negligible during times as short as 10^{-9} second.[1] The ion current density j_p, which is proportional to the plasma density, therefore stays constant.

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* Part of this research was supported by the U. S. Air Force through the Office of Scientific Research of the Air Research and Development Command.

[1] K. G. Hernqvist, J. Appl. Phys. 27, 1226 (1956).

[2] R. H. Fowler and L. W. Nordheim, Proc. Roy. Soc. (London) A119, 173 (1928).

[3] S. S. Mackeown, Phys. Rev. 34, 611 (1929).

[4] T. Wasserrab, Z. Physik 130, 311 (1951).

[5] D. Roller, Phys. Rev. 36, 738 (1930).

[6] K. D. Froome, Proc. (Phys. Soc. London) 60, 424 (1948); 62, 805 (1949); and 63, 377 (1950).

[7] L. Tonks, Physica 6, 294 (1935).

[8] C. G. Smith, Brit. J. Appl. Phys. 4, 252 (1953).

[9] G. Mierdel, Z. tech. Phys. 17, 452 (1936).

[10] O. Engelbrecht, Arch. Elektrotech. 36, 515 (1942).

Thus if the electric field at the cathode surface is maintained only by positive ions generated in the plasma, this field would be at least as large after arc extinguishing as before. Thus it is seen that the Mackeown theory also fails to give a satisfactory answer to the question of the short extinguishing time.

Because of the importance of the emission current density for an understanding of the emission mechanism of cold cathode arcs this paper deals primarily with studies of the *D* type of arc. The implications of these studies for the mercury pool arc are discussed.

II. DISPERSED TYPE OF COLD CATHODE ARC

1. Methods of Establishing the Arc

The basic electrode geometry for the *D* type of arc is illustrated in Fig. 1. A cylindrical pure molybdenum electrode having a slightly rounded top, protrudes through the surface of the pool of mercury, with the top surface of the electrode about 1 centimeter below a cylindrical stainless steel anode. An electromagnet provides a variable magnetic field (up to 7000 gauss) oriented parallel to the axis of the two electrodes. The mercury pool communicates with a reservoir through a manometer arrangement, permitting adjustment of the mercury level with respect to the top surface of the molybdenum electrode. During normal operation the tube is continuously pumped.

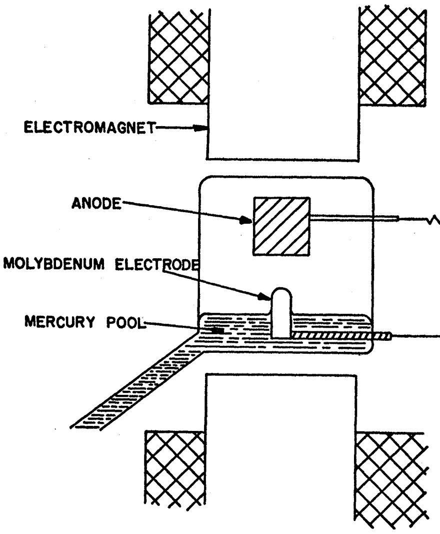

FIG. 1. Basic set-up for activation and operation of the *D* type of cold-cathode arc discharge.

When first immersed in the mercury pool, the molybdenum electrode is not wetted by the mercury, the meniscus being bent downwards as shown in Fig. 2. A hydrogen glow discharge is first operated in the tube. After this cleaning operation the electrode is completely wetted, the meniscus being bent upwards, as shown in Fig. 2. When the arc is started the cathode spot anchors at the meniscus and encircles the electrode with a bright ring of light. A magnetic field of a few thousand gauss can now be turned on without extinguishing the arc. This type of discharge [Fig. 3(a)] in the presence of a parallel magnetic field appears to be quite stable, and is the one which is normally encountered. The *D* type of arc cannot be obtained under these conditions.

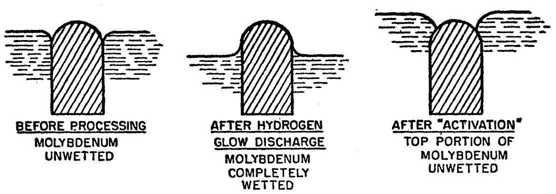

FIG. 2. Shape of mercury meniscus.

The process hereafter taking place is a quite tedious one requiring several hours of operation of the dc arc in the presence of the magnetic field. A condition is eventually obtained when a slowly increasing area at the top surface of the molybdenum electrode appears to be unwetted by the mercury. Presumably the intense ion bombardment uncovers parts of the bare molybdenum surface leaving it exposed to the residual gases present in the tube. Eventually this unwetted area extends down to the wetting line at which the arc is anchored. The arc can no longer operate stably in its normal mode, the bright circular cathode line suddenly leaves the meniscus boundary, hops up onto the unwetted top surface of the molybdenum electrode and spreads out uniformly over a large area, as shown in Fig. 3(b). The molybdenum electrode appears to be wet with mercury except for the top surface which appears to be unwetted, the meniscus being bent downwards as shown in Fig. 2.

Once established, the *D* type of arc appears to be quite stable over a wide range of magnetic fields (1000–7000 gauss) and anode currents (2 to 6 amperes). The *D* type of arc requires an arc drop of about 14 volts as compared to 10 volts for the normal mode. Oscillographic observations of the arc drop indicates noise

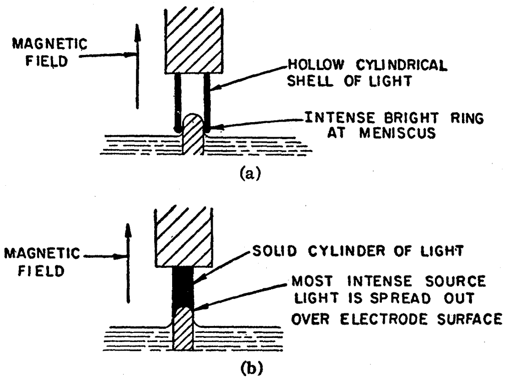

FIG. 3. (a) Arc operating in "normal" mode with magnetic field applied parallel to discharge. (b) Arc operating in "dispersed" mode with magnetic field applied parallel to discharge.

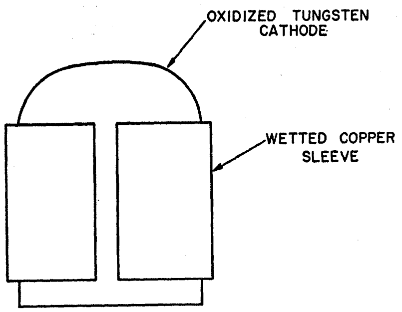

FIG. 4. Cathode for *D* type of arc.

components of an amplitude approximately 2% of the average arc drop. The frequency spectrum of the noise has a quite sharp maximum at about 10 megacycles per second due to more or less coherent oscillations. As long as the side surfaces of the molybdenum electrode are well wetted with mercury the meniscus level of the mercury pool can be brought down as much as 1 cm from the top surface, however the mercury pool cannot be completely removed from the tube without extinguishing the arc. Presumably the presence of mercury in the vicinity of the discharge region is necessary to maintain sufficient vapor pressure. From the temperature of the mercury pool the vapor pressure is estimated to be about 1 mm of Hg.

It seemed quite probable that the process of establishing the *D* type of arc described above involves an oxidation of the top surface of the molybdenum electrode by the residual oxygen in the tube while keeping the sides of the electrode wetted for anchoring of the arc in its normal mode. Therefore a cathode was prepared based on the following principles: (1) The cathode work function must be high. (2) Means for anchoring of the arc in its normal mode must be provided. (3) The arc must be made unstable in its normal mode when a longitudinal magnetic field is applied.

In Fig. 4 is shown a cathode structure based on these principles. The cathode is made of tungsten whose top surface is polished and oxidized in air to yield a high work-function surface[11,12] ($\phi > 6$ volts). For anchoring of the arc cathode spot, a sleeve of copper wetted with mercury is mounted on the tungsten electrode as shown in Fig. 4. In order to break up the wetting line, a slit is cut in the copper sleeve, as shown. This tends to make the arc unstable in its normal mode when the magnetic field is applied, thus causing a mode jump. The electrode was partly immersed in a mercury pool in a manner similar to the molybdenum electrode described above. When the arc was fired, the cathode spot anchored at the copper sleeve. When the magnetic field was applied the arc turned immediately into the *D* type of operation. Thus it has been shown that the emission of the *D* type of arc occurs from an oxidized metal surface. The mercury pool only serves to provide a sufficient vapor pressure for the discharge.

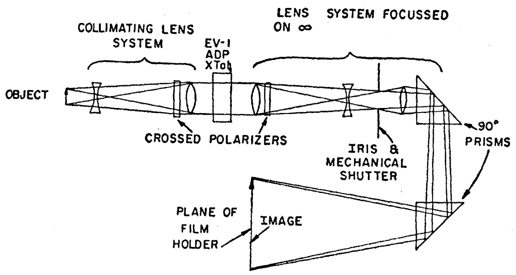

FIG. 5. Optical arrangement of ultra-high-speed camera.

2. Ultrahigh-Speed Photographic Studies

It is important to determine whether the electron emission in the *D* type of arc is uniform over the cathode surface, or occurs from rapidly moving spots or spots of short lifetime such as to give the illusion of uniformity as observed by the naked eye. Therefore, ultrahigh-speed photographic studies of the cathode surface were undertaken.

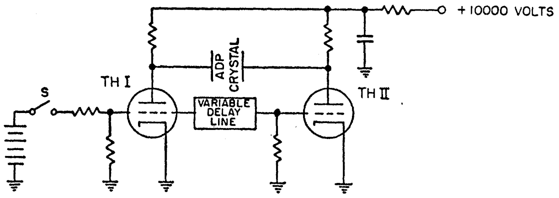

FIG. 6. Schematic diagram of circuit for electro-optical shutter.

The optical arrangement of the camera used is shown in Fig. 5. The high-speed shutter consists of a Baird Associates model EV-1 Electro-Optic Light Modulator mounted between a pair of crossed linear polarizers. The basic unit is a plate of ammonium-dihydrogen-phosphate (ADP-crystal) placed between a pair of electrodes which allow light to pass in the same direction as the electric field between the electrodes. To open the shutter a high-voltage pulse is applied across the crystal for the duration of the exposure. A mechanical shutter is placed in series with the electrical shutter, as shown. The pulse equipment which opens the crystal shutter for the desired exposure time is synchronized with the mechanical shutter, which opens for 1/400 of a second. Since the electro-optic shutter is not perfect (it leaks considerable light even when closed), the mechanical shutter is essential in order to minimize the exposure of film due to leakage light. The lower limit of exposure time (about 10 microseconds) is determined by the leakage light through the electro-optic shutter while the mechanical shutter is open.

Figure 6 shows schematically the electrical circuit that was used for opening the electro-optical shutter. The electrodes of the ADP crystal were connected

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[11] R. C. L. Bosworth and E. K. Rideal, Proc. Roy. Soc. (London) A162, 1 (1937).

[12] K. H. Kingdon, Phys. Rev. 24, 510 (1922).

between the plates of two 5C22 hydrogen thyratrons. The first thyratron, Th I, was triggered directly by the flash synchronizing contact S of the mechanical shutter. When Th I fires, its plate attains ground potential and the B voltage (10 kv) appears across the ADP crystal. The triggering signal is transmitted through the variable delay line, which determines the exposure time, to Th II. When Th II fires, its plate potential also attains ground potential, thus removing the potential across the ADP crystal.

Photographs were taken of the cathode surface of the D type of arc, using exposure times ranging from 10 to 1000 microseconds. One of these is shown in Fig. 7. The arc current was 6.5 amperes and the cathode area (top surface of the molybdenum electrode) was approximately 0.39 cm^2. The photographs at different exposure times only show a difference in intensity of exposure. They show that the light emitted at the cathode is uniformly distributed over the whole cathode surface. No bright spots or graininess of the light emitted could be found in any of the pictures taken.

Based on these photographic studies, the following two possibilities may be considered:

(*a*) A small fast-moving cathode spot scans the whole cathode surface in 10 microseconds. Assume that an emission area (of diameter d) scans the cathode surface in an orderly fashion. If the spot velocity is v then the time τ to scan the cathode surface is

$$\tau = D^2/vd, \tag{4}$$

where D^2 is the area of the cathode surface. If the emission current is I, one obtains from (4) an upper limit to the current density j_e:

$$j_e \leq I(\tau v/D^2)^2. \tag{5}$$

Studies of cathode-spot motion[6,13] indicate that $v < 10^5$ cm/sec. Thus using the results from the photographic studies one obtains from (5) $j_e \leq 40$ amperes/cm^2.

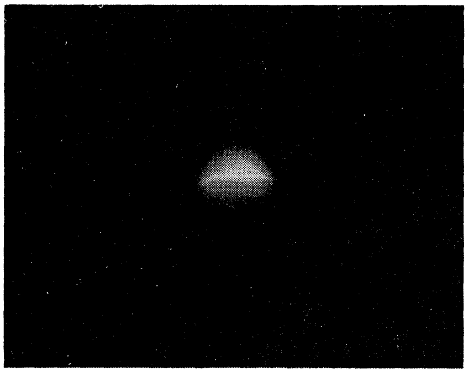

FIG. 7. Photograph of the cathode surface of the D type of arc taken with the camera inclined about 30° from the horizontal axis. The bright curved line is the outline of the cathode surface with some of the bright discharge column visible above. Exposure time = 1000 microseconds.

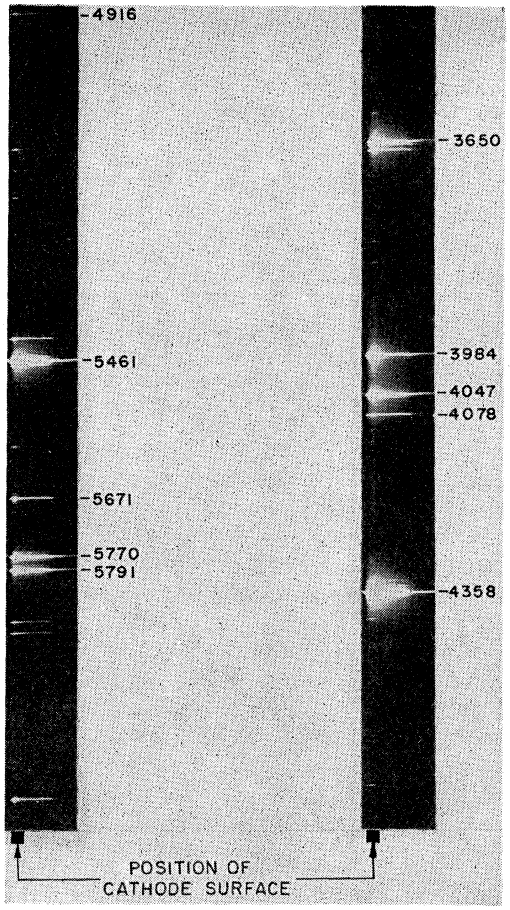

FIG. 8. Spectrum of the D type of arc.

(*b*) Emission occurs from small spots of short lifetime. Assume a spot lifetime t. The shortest time τ to cover the whole cathode uniformly with light is then

$$\tau = (D^2/d^2)t, \tag{6}$$

or

$$j_e \leq I\tau/D^2 t. \tag{7}$$

Studies of plasma density decay[1] of the mercury pool arc indicate that $t \approx 1$ microsecond and thus from (7) $j_e \leq 150$ amperes/cm^2.

Assuming that the light originating at the cathode surface is a true measure of the distribution of electron emission current density it must be concluded from these measurements that the emission current density of the D type of arc is at least as low as 150 amperes/cm^2 and may be as low as 20 amperes/cm^2. The electric field at the cathode surface calculated from (1) is then only 4×10^3 volts/cm. The Mackeown theory then cannot account for the large field necessary for field emission.

3. Spectrographic Studies

A possible way to obtain information about the electric field strength at the cathode surface is to study

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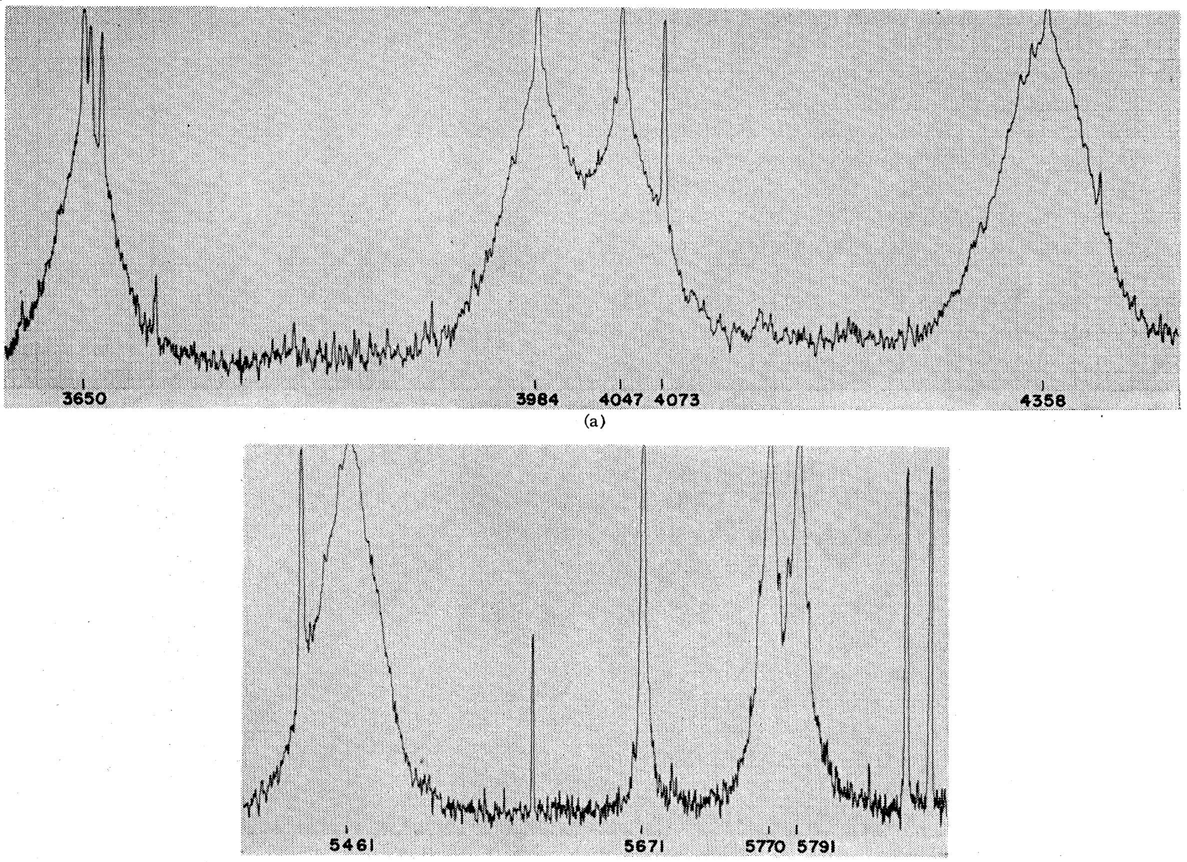
[13] R. M. St. John and J. G. Winans, Phys. Rev. **98**, 1664 (1955).



(a)

(b)

FIG. 9. Densitometer trace of Fig. 8.

the spectrum of the radiation originating in this region. In the presence of the nonuniform electric field, a considerable broadening of the spectrum lines occurs due to the Stark effect. If the Stark shift *versus* electric field relation is known, the maximum field strength at the cathode surface can be estimated. Such studies were made by St. John and Winans[13] for an anchored mercury pool arc. Both symmetric and asymmetric broadening were observed in agreement with the known Stark shift. The observed Stark shift indicated an electric field strength at the cathode surface which is much higher than that calculated from (1) using a value of $j_e = 10\,000$ amp/cm^2 as measured by Tonks.[7]

Spectrographic studies were made of the *D* type of arc. The spectrum emanating from the cathode surface is shown in Fig. 8. Figure 9 shows a densitometer trace of Fig. 8. The following results were obtained from these studies: (1) There is no essential difference in the spectrum originating from the cathode surface and from the main discharge plasma. (2) The broadening of the lines is symmetric and much less than in the spectrum of an anchored mercury pool arc.[13] This indicates that the conditions at the cathode surface of the *D* type of arc may be different from those of a normal mercury pool arc.

4. Transient Behavior of the Arc

To study the transient behavior of the arc, the following experiment was performed on a *D* type of arc. A short negative voltage pulse was applied to a running dc arc. The arc current and voltage were observed on oscilloscopes. It was found that during the application of the pulse the arc current approached zero as the anode voltage approached a value (5 to 6 volts) slightly higher than the work function of the anode. When the arc current reached the value zero the arc extinguished. No attempt was made to determine the minimum extinguishing time because at short pulse lengths such measurements are extremely difficult to perform due to the variation and noisiness of the arc current and voltage. However, it was determined that the extinguishing time is less than $\frac{1}{2}$ microsecond.

It appears that the transient behavior of the *D* type of arc is quite similar to that of a mercury pool arc.[1,9,10]

5. Theory of the Emission Mechanism of the *D* Type of Arc

From the experiments on the *D* type of arc described above the following conclusions may be drawn: (1) The electron emission in the *D* type of arc occurs from an oxidized metal surface of high work function. The D type of arc must therefore be regarded as a specific form of cold cathode arc and not as a special mode of the mercury pool arc. (2) The low emission current density of the D type of arc makes it possible to say with certainty that the ion flow from the plasma to the cathode cannot support an electric field at the cathode sufficient for field emission. This is corroborated by the spectrographic studies. (3) Studies of the transient behavior of the D type of arc have suggested that the emission mechanism is similar to that of field emission.

In view of the apparent contradiction of these conclusions a different source of positive ions must be sought: a source which can provide an electric field at the cathode sufficient for field emission. It is suggested here that the supply of ions is due to excited atoms which undergo resonance ionization at the cathode surface.

Consider a cathode of a cold-cathode arc as shown in Fig. 10. Ions generated in the plasma will flow to the cathode giving rise to a positive ion space-charge sheath between the plasma and the cathode. The corresponding potential distribution is shown in Fig. 10, the electric field at the cathode surface being given by Eq. (1). Provided that $(m_p/m_e)^{\frac{1}{2}} \gg j_e/j_p$, the space-charge sheath thickness d in cm is given approximately by

$$d^2 \cong 2.33\times10^{-6}\left(\frac{m_e}{m_p}\right)^{\frac{1}{2}}\frac{V_c^{\frac{3}{2}}}{j_p}, \qquad (8)$$

where V_c is the cathode drop in volts. In addition to the ions, a large number of excited atoms is generated in the plasma. Because of thermal diffusion some of these excited atoms will travel towards the cathode surface. If the lifetime of the excited atoms is long enough they will travel through the space-charge sheath and reach the cathode. The process[14] taking place when the excited atom reaches the cathode depends on whether the cathode work function ϕ is smaller than or larger than the difference between the ionization and excitation potential of the atom $(V_i - V_{\text{ex}})$. (1) If $\phi < V_i - V_{\text{ex}}$, the excited atoms will most likely be de-excited resulting in Auger ejection of electrons from the cathode. The yield of electrons per excited atom may approach unity. (2) If $\phi > V_i - V_{\text{ex}}$, the process of resonance ionization of the excited atom is most likely.[15] In this process an electron is ejected from the excited atom into the cathode and thus an ion with only thermal velocity is generated close to the cathode surface. If the lifetime of the ions is sufficiently long, a layer of positive ions may be generated at the cathode surface. These ions may give rise to the field emission of a large number of electrons in a manner similar to that in the Malter effect.[16]

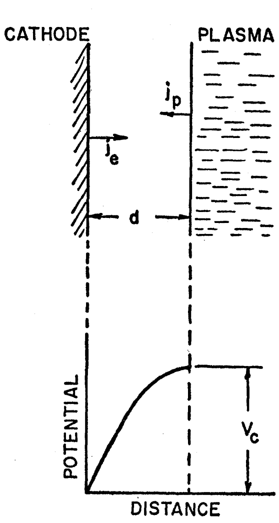


FIG. 10. Potential distribution between plasma and cathode of a cold-cathode arc.

Since the excited atoms are generated in the plasma, they must have a long lifetime in order to penetrate the sheath and reach the cathode. Except for extremely large current densities (thin sheaths), this requirement is fulfilled only for metastable states. If the lifetime of excited atoms is τ_{ex}, then the mean distance travelled by excited atoms is $\tau_{\text{ex}}\bar{c}$, where $\bar{c}$ is the average thermal velocity of the atoms. Thus the effects of resonance ionization on the electron emission may be expected to occur only under the following conditions: (1) $\phi > V_i - V_{\text{ex}}$, where V_{ex} refers to a metastable state, and (2) $d \leq \tau_{\text{ex}}\bar{c}$.

It is easily seen that these conditions are indeed satisfied for the D type of arc operated in a mercury vapor. For mercury vapor the two metastable states $6\,{}^3P_2$ and $6\,{}^3P_0$ have $V_i - V_{\text{ex}}$ equal to 4.95 and 5.72 volts, respectively. Oxidized tungsten[11,12] is known to have a work function ϕ larger than 6 volts, thus satisfying the condition $\phi > V_i - V_{\text{ex}}$. For the D type of arc $V_c = 14$ volts, $j_e = 10$ amp/cm^2 and $j_e/j_p = 50$, yielding $d \approx 10^{-3}$ cm from (8). Assuming $\bar{c} \approx 10^4$ cm/sec, the requirement $d \leq \tau_{\text{ex}}\bar{c}$ yields $\tau_{\text{ex}} \geq 10^{-7}$ sec. This requirement is certainly fulfilled for the metastable atoms of mercury[17] moving through the space-charge sheath.

For a quantitative evaluation of the proposed emission mechanism, the following quantities must be considered: (1) the density of excited states in the plasma, N_x cm^{-3}; (2) the fraction of excited atoms which undergo resonance ionization at the cathode, κ; (3) the lifetime of ions generated at the cathode surface, τ_p sec; and (4) the number of electrons emitted from the cathode per second per ion, η.

Under the assumption that the lifetime of the excited state is larger than the transit time of the atom through the space-charge sheath, the influx of excited atoms to the cathode surface is given by

$$\Gamma_{\text{ex}} = N_x\bar{c}/4 \text{ atoms per second per cm}^2. \qquad (9)$$

With the above-defined quantities, one obtains the

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[14] H. D. Hagstrum, Phys. Rev. **96**, 336 (1954).

[15] A. Bühl, Helv. Phys. Acta **6**, 231 (1933).

[16] L. Malter, Phys. Rev. **50**, 48 (1936).

[17] C. Kenty, J. Appl. Phys. **21**, 1309 (1950).

electron emission current density,

$$j_e = e(N_x \bar{c}/4)\kappa\tau_p\eta, \tag{10}$$

where e is the electronic charge. Since the ion current density is given by

$$j_p = e(N\bar{c}/4), \tag{11}$$

Eq. (10) can be written

$$j_e/j_p = \kappa\tau_p\eta(N_x/N). \tag{12}$$

Here N is the plasma density in cm^{-3}.

In considering Eq. (12), certain limits must be imposed on the electron-to-ion current density ratio j_e/j_p. An upper limit is $j_e/j_p \leq (m_p/m_e)^{\frac{1}{2}}$ at which the electron current from the cathode is space-charge limited. A lower limit is set by the plasma energy-balance requirements. The energy-balance equation can be written as[1]

$$V_A = \phi_A + \frac{P_{\mathrm{ex}}}{I_A} + \frac{I_p}{I_A}(V_i + V_A - \phi_A + \phi_c) + 2\frac{kT_e}{e}, \tag{13}$$

where V_A = anode voltage, I_A = anode current, ϕ_A = work function of the anode, I_p = ion current flowing to the cathode, I_e = electron current flowing from the cathode, ϕ_c = work function of the cathode, P_{ex} = power lost in generating excited atoms, k = Boltzmann constant, and T_e = electron plasma temperature. Since $I_A = I_e + I_p$ and $I_e/I_p \cong j_e/j_p$, Eq. (13) can be written as

$$P_{\mathrm{ex}} \cong I_p\left[\left(V_A - \phi_A - 2\frac{kT_e}{e}\right)\left(\frac{j_e}{j_p} + 1\right) - (V_i + V_A - \phi_A + \phi_c)\right]. \tag{14}$$

Part of the power P_{ex} is lost in radiation from the discharge. Write this part as a fraction x of the total power input to the tube or xV_AI_A. Another part of P_{ex} supplies the influx of excited atoms to the cathode. From Eqs. (9) and (11), one can therefore write

$$P_{\mathrm{ex}} > V_{\mathrm{ex}}(N_x/N)I_p + xI_AV_A. \tag{15}$$

Equations (14) and (15) give a lower limit of j_e/j_p or

$$\frac{V_{\mathrm{ex}}(N_x/N) + V_i + V_A - \phi_A + \phi_c}{V_A - \phi_A - 2\frac{kT_{\mathrm{e}}}{e} - xV_A} < \frac{j_e}{j_p} < \left(\frac{m_p}{m_e}\right)^{\frac{1}{2}}. \tag{16}$$

Assuming a Maxwellian velocity distribution for the plasma electrons, the population of excited atoms can be written as[17]

$$N_x = 4\pi\left(\frac{m_e}{2\pi kT_e}\right)^{\frac{3}{2}} N_a N \sum_{\alpha} \tau_\alpha 2\times 10^{14}\frac{e^2}{m_e^{\,2}} \times \int_0^\infty q_\alpha(V)V\exp(-10^7 eV/kT_e)dV, \tag{17}$$

where the sum is to be taken over the α excited states considered. Here N_a = density of neutral gas, τ_α = the mean life of the state α, and $q_\alpha(V)$ = atomic cross section for excitation of the state α by an electron of V electron volt energy. No attempt will be made here to analyze in detail the effects of transition between excited states. For mercury the two metastable states $6\,^3P_2$ and $6\,^3P_0$ are of primary interest. For these states one finds from Eq. (17) and known values[17] of $q(V)$, for an electron temperature of 15 000°K,

$$N_x/N \cong 4\times 10^7[\tau_2 + 0.2\tau_0]p. \tag{18}$$

Here τ_2 and τ_0 are the mean lifetimes of the $6\,^3P_2$ and the $6\,^3P_0$ states, respectively, and p is the gas pressure. At the current density used in the D type of arc (10 amp/cm^2 or higher) the lifetimes of the metastable states are primarily determined by quenching by electrons.[17,18] From the current density, the plasma density N of the D type of arc can be estimated to be of the order of 10^{13} cm^{-3}. Taking Kenty's data[17] of $\tau_2 = 4\times 10^{-5}$ sec, $\tau_0 = 6\times 10^{-5}$ sec for $N = 2.1\times 10^{11}$ cm^{-3}, one obtains for the D type of arc under the assumption that τ_α is inversely proportional to N, $\tau_2 = 2\times 10^{-7}$ sec, and $\tau_0 = 3\times 10^{-7}$ sec. Finally, from (18) and assuming $p = 1$ mm of Hg, one obtains $N_x/N \approx 10$.

Returning now to relation (16), one finds for the D type of arc in mercury vapor $V_{\mathrm{ex}} \approx 5$ volts, $N_x/N \approx 10$, $V_i \approx 10$ volts, $V_A = 14$ volts, $\phi_c \approx 6$ volts, $\phi_A \approx 4.5$ volts, and $2(kT_e/e) \approx 3$ volts. The lower limit of j_e/j_p is shown in Table I as a function of x. Thus it is seen that j_e/j_p cannot be less than about 10, but, since it must be assumed that at least 25% of the input power is lost in radiation, j_e/j_p is more likely to be of the order of 50 which is a value found for the ordinary mercury pool arc.[1]

Very little is known about the actual value of the ion yield of resonance ionization κ. The effect has been experimentally observed by Bühl[15] for metastable mercury atoms. No data on yield have been reported. However, since under the condition $\phi_c > V_i - V_{\mathrm{ex}}$ the probability for Auger de-excitation is very much less than for resonance ionization,[14] it seems reasonable to assume that the yield κ is not much less than unity.

The factors τ_p and η are extremely difficult to evaluate. However, the product $\tau_p\eta$ is intimately connected with the secondary emission yield due to the Malter effect.[16] For the Malter effect, positive charges are

TABLE I. Electron-to-ion current ratio j_e/j_p *versus* fractional energy lost in radiation x as determined by Eq. (16).

x	j_e/j_p
0	11.8
0.1	15
0.2	20.7
0.3	33.3
0.4	76.5

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[18] H. Kopfermann and R. Ladenburg, Naturwiss. **19**, 513 (1931).

created in a metallic film on top of an oxidized cathode by secondary electron emission. Considering Eq. (12) and assuming $j_e/j_p \approx 50$, $\kappa \approx 1$, and $N_x/N \approx 10$, one finds $\tau_p \eta \approx 5$. A yield of this order of magnitude is quite modest for the Malter effect. Thus the proposed emission mechanism for the *D* type of arc appears to be acceptable from order of magnitude considerations.

It is seen from Eq. (18) that in order to obtain a sufficiently high value for N_x/N, the pressure p must be large. This is believed to be the reason why the mercury pool must be in close contact with the cathode electrode, thus providing a sufficient evaporation rate.

A satisfactory theory for the emission mechanism of cold-cathode arcs must provide an explanation for the short arc-extinguishing time. As mentioned in Sec. I, the Mackeown space-charge sheath theory cannot account for this effect, since plasma decay is negligible during times less than one microsecond.[1] However, there are two plasma parameters that may change in such a short time upon current interruption. The first one is the electron temperature. As will be shown in Sec. III.2, electron cooling is very rapid due to evaporation of fast electrons from the plasma and due to inelastic collisions of the fast electrons. This results in an immediate reduction in the generation rate of excited atoms. The population of excited atoms in the plasma will therefore decay in times which may be of the order of $\tau_{\text{ex}} = 3 \times 10^{-7}$ sec for the *D* type of arc. Furthermore a very rapid decay of the number of ions present at the cathode surface must be expected when the electron emission is quenched. A similar behavior is observed for the Malter effect.[16] For the *D* type of arc the buildup time of ions at the cathode surface must be considered. This time, of course, is of the order of τ_p. The following two cases must be considered: (1) $\tau_p > \tau_{\text{ex}}$. In this case, which is probably the more likely one, the population of excited states has decayed before a positive-ion layer has had time to build up at the cathode surface and the extinguishing time is immeasurably small. (2) $\tau_p < \tau_{\text{ex}}$. In this case the extinguishing time would be of the order of τ_x or about 3×10^{-7} sec for the *D*-type of arc.

In Table II are shown some of the assumptions and conclusions drawn from the proposed theory for the emission mechanism of the *D* type of arc together with their experimental corroborations.

TABLE II. Theoretical postulates and experimental verification for the proposed emission mechanism of the *D* type of arc.

Theory	Experiment
Field emission	$I_A \rightarrow 0$ as $V_A \rightarrow \phi_A$
Not a mode of the mercury pool arc	Emission area not wetted by mercury
Space-charge sheath theory inadequate	Low current density and spectroscopic studies
Cathode work function high	Oxidized metal surface
Insulating film on surface	Oxidized metal surface
$\phi > V_i - V_{\text{ex}}$	Satisfied for metastable states of mercury and oxidized tungsten surface
$d < \tau_{\text{ex}} \bar{c}$	Satisfied in the *D* type of arc
Pressure must be sufficiently high to make N_x/N large	Mercury pool must be in close contact with the cathode electrode
Extinguishing time $\leq 3 \times 10^{-7}$ sec	Extinguishing time $< 5 \times 10^{-7}$ sec

III. THE MERCURY POOL ARC

1. Emission Mechanism

In Sec. II.5 it was pointed out that the *D* type of arc must not be considered as a special mode of the mercury pool arc since emission occurs from an oxidized metal cathode of high work function. However, there are sufficient similarities between the two phenomena to warrant certain conclusions concerning the mercury pool arc: For both types of arc, pulse measurements indicate some sort of field emission mechanism. In neither case can the ions generated in the plasma provide a sufficiently high field at the cathode surface to yield field emission. Both arcs exhibit the phenomenon of a very short extinguishing time, which cannot be accounted for by the space-charge sheath theory.

Spectrographic studies by St. John and Winans[13] on the mercury pool arc have indicated that the field at the cathode surface is much larger than can be accounted for by the Mackeown space-charge sheath theory. *Therefore other sources of ions must be looked for which can provide more positive space charge at the cathode surface.* One such source of ions may be excited atoms which are generated in the plasma and become ionized in the space-charge sheath. In applying these ideas to the mercury pool arc, the following facts are of importance: (1) The current density of the mercury pool arc is very much higher than for the *D* type of arc. Consequently the cathode field E_c as determined by Eq. (1) is very high though presumably not high enough for field emission. Also the sheath thickness d is very small. (2) The work function of the mercury pool is only 4.52 volts and there is no insulating film at the emitting area. (3) The plasma density is very high due to the high current density ($N \approx 10^{15}$ cm^{-3}). This yields a very short mean life τ_{ex} even for metastable states due to quenching by electrons. (4) The vapor pressure adjacent to the cathode surface is very high, possibly of the order of hundreds of mm of Hg.[19] (5) The complicated pressure and geometry conditions make an evaluation of the emission phenomena of the mercury pool arc very difficult. Owing to the high plasma density, the lifetimes of all excited states may be expected to be in the range 10^{-8} to 10^{-9} second for the plasma of the mercury pool arc. However, as seen from Eq. (18) this is counteracted by the higher vapor pressure to give about the same population of excited states as for the *D* type of arc.

One effect of excited atoms to be considered is

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[19] J. Rothstein, Phys. Rev. 73, 1214 (1948).

resonance ionization at the cathode surface. Since the work function of mercury is 4.52, the criterion $\phi_c > V_i - V_{\text{ex}}$ is fulfilled only for states higher than the 6 $^3P_2$ state. Because of the thin sheath thickness d, even ordinary excited atoms may reach the cathode surface. A calculation of the transition rate from the 6 $^3P_1$ to the 7 $^3S_1$ using the known cross section for this process[17,20] indicates that the population of the 7 $^3S_1$ state may be of the same order of magnitude as the plasma density. This, then, represents a possible source for ion generation near the cathode surface. A second effect to be considered is the ionization of excited atoms due to the strong electric field near the cathode surface.[21] This field, which may be of the order of 10^6 to 10^7 volts/cm for the mercury pool arc,[13] may be sufficient to ionize a fraction of the excited atoms penetrating the space-charge sheath. The ions generated by these processes will spend much longer times in the immediate vicinity of the cathode surface than the ions generated in the main plasma. Newton[22] has shown that individual ions in the strong average electric field may give rise to the emission of a large number of electrons provided that the ions are moving slowly in the immediate vicinity of the cathode surface.

A different way in which excited atoms may contribute to the emission has been suggested by Robson and von Engel.[23] This is the mechanism of Auger ejection of electrons due to excited atoms approaching the cathode. There are several reasons, however, why this mechanism of electron emission is unlikely to be the exclusive one. For the states 6 $^3P_0$, 6 $^3P_1$, and 6 $^3P_0$, which would be the most important ones, the yield of emitted electrons per excited atom cannot exceed unity. However, unless the generation rate of excited atoms were much higher for the mercury pool arc than for the D type of arc, it is seen from Eq. (12) that the yield must be larger than one, taking the measured value of $j_e/j_p = 50$ and the calculated value of $N_x/N = 10$. On the other hand, it is difficult to conceive that more than half of the excited atoms can diffuse to the cathode. Assume that the most favorable case in which all energy input to the tube goes into formation of excited atoms and that the yield be one. In this case the anode voltage V_A must be at least equal to double the excitation potential or about 9.8 volts for mercury. However, it is known[24] that the mercury pool arc operates at anode voltages as low as 7 to 8 volts. Thus, although the effect of Auger ejection of electrons may be important, it is probably not the exclusive one.

2. Extinguishing Time of the Mercury Pool Arc

A crucial test of a theory for the emission mechanism of the mercury pool arc is its ability to account for the short extinguishing time as discussed in Sec. I. It will be shown in this section that if the excited atoms play a predominant role in the emission mechanism, a very short extinguishing time should be expected. This is due to the rapid decrease in the production rate and population of excited atoms during arc-current interruption.

The decrease of population of excited atoms is determined by the mean life τ_{ex}. Since the plasma density of the mercury pool arc is several orders of magnitude higher than for the D type of arc, τ_{ex} may be expected to be of the order of magnitude 10^{-8} to 10^{-9} second for *all* excited states.

The production of excited atoms depends very critically on the electron temperature since T_e enters as an exponential factor in Eq. (17). For instance, a drop in the electron temperature from 15 000 to 11 100°K will lower the production rate of the 6 $^3P_2$ state by a factor of about 4. Thus one need only consider the first very fast drop in electron temperature. This initial fast change of the electron temperature is due to two effects, one being inelastic collisions and the other evaporation cooling of the electron gas. These two effects result in a rapid speed reduction and a removal of the fast electrons of the Maxwellian velocity distribution respectively.

In evaluating the effects of inelastic collisions, the excitation of the 6 $^3P_0$, 6 $^3P_1$, and 6 $^3P_2$ for mercury will be considered. Let the sum of cross sections for such collisions be $q(V)$. The mean time between collisions of this kind τ_c can be written as

$$\tau_c = \frac{1}{5.95\times10^7 V^{\frac{1}{2}} q(V) N_a}. \tag{18}$$

From the known value[17] of $q(V)$ the collision time τ_c is as shown in Table III as a function of the electron energy V in electron volts at a vapor pressure of 1 mm of Hg. It is seen that τ_c is of the order 10^{-9} to 10^{-8} second for a vapor pressure of 1 mm of Hg, which would

TABLE III. Mean collision time τ_c for inelastic collisions in mercury vapor at a pressure of 1 mm of Hg as a function of electron energy V in electron volts.

V ev	τ_c Millimicroseconds
5	4.7
5.2	2.1
5.5	0.91
6	0.51
6.5	0.45
7	0.45
7.5	0.45
8	0.49

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[20] B. Yavorsky, Compt. rend. **48**, 175 (1945).

[21] C. Lanczos, Z. Physik **65**, 431 (1930); **68**, 204 (1931).

[22] R. R. Newton, Phys. Rev. **73**, 1122 (1948).

[23] A. E. Robson and A. von Engel, Nature **178**, 646 (1955).

[24] M. J. Druyvesteyn and F. M. Penning, Revs. Modern Phys. **12**, 87 (1940).

apply to the D type of arc. For the mercury pool arc τ_c is one or two orders of magnitude lower due to the higher vapor pressure. After the time τ_c most of the energy carried by the fast electrons has been removed from the electron gas. This however does not imply that there is no excitation occurring after the time τ_c. Because of the high plasma density it must be assumed that the relaxation time of the electron gas is sufficiently short to allow a continuous redistribution of the velocity distribution to a Maxwellian distribution. Assuming that after a time τ_c all electrons of velocity larger than v_x of the original velocity distribution have lost their energy and that the energy redistribution occurs entirely within the electron gas, one obtains

$$\frac{T_{e1}}{T_{e0}}=\frac{\int_0^{v_x}\tfrac{1}{2}m_ev^2\exp[-\tfrac{1}{2}(m_ev^2/kT_{e0})]v^2dv}{\int_0^{\infty}\tfrac{1}{2}m_ev^2\exp[-\tfrac{1}{2}(m_ev^2/kT_{e0})]v^2dv}$$

$$=\int_0^{z_x}ze^{-z}dz\Big/\int_0^{\infty}ze^{-z}dz, \qquad (19)$$

where T_{e0} is the initial electron temperature, T_{e1} is the electron temperature after τ_c, and $z_x=\tfrac{1}{2}(m_ev_x^2/kT_{e0})$. Equation (19) can be written in terms of the incomplete factorial function[25] as

$$\frac{T_{e1}}{T_{e0}}=\frac{(1,\,11\,600V_x/T_{e0})!}{(1,\,\infty)!}, \qquad (20)$$

where $V_x=m_ev_x^2/2e$. Thus the electron temperature T_{e_n} after a time $n\tau_c$ is

$$T_{e_n}=T_{e0}\prod_n\frac{(1,\,11\,600V_x/T_{e_n})!}{(1,\,\infty)!}. \qquad (21)$$

As an example, in Fig. 11 we have plotted the electron temperature as a function of multiples of τ_c assuming $T_{e0}=15\,000$°K and $V_x=5$ volts. It is seen that the electron temperature has fallen below 11 000°K after $5\tau_c$. After this time the electron temperature falls off more slowly until elastic collisions become the more important factor in cooling of the electron gas.

Contrary to the above-discussed effect, the evaporation cooling is due to a preferential *removal* of the fast electrons of the plasma. In the arc-extinguishing experiment, the anode voltage is suddenly reduced to 5 to 6 volts for a time τ. This makes it possible for the fast electrons to climb the potential hill at the cathode edge of the plasma and escape to the cathode. In order to preserve charge neutrality of the plasma, this electron current to the cathode must be equal to the ion current. The total number of electrons escaping from the plasma is therefore equal to $\tau(I_p/e)$, where I_p is the ion current flowing to the cathode at the dc arc. The actual energy loss of the electron gas then depends critically on the size of the discharge plasma. In view of Eq. (11) the fractional loss to the total number of electrons of the plasma is

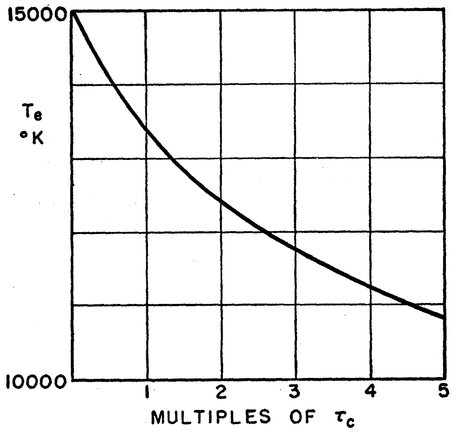

FIG. 11. Electron temperature T_e as a function of multiples of τ_c.

$$\Delta n/n=\tau(\bar{c}/4D), \qquad (22)$$

where D is the plasma thickness. Taking an experimental value[26] of $D=4\times10^{-3}$ cm for the mercury pool arc and assuming $\bar{c}=2\times10^4$ cm/sec, Eq. (22) yields $\Delta n/n\approx1\%$ for $\tau=10^{-8}$ sec. This corresponds to a temperature reduction of several thousand degrees for a 15 000°K plasma.

Thus it is seen that if the excited atoms play a predominant role in the emission mechanism of the mercury pool arc, an arc-extinguishing time of the order of 10^{-9} to 10^{-8} second should be expected.

CONCLUSIONS

The D type of arc operates in mercury vapor. The cathode consists of an oxidized metal surface of high work-function. The emission current density is as low as 10–100 amperes per square centimeter which indicates that the high electric field at the cathode surface necessary for field emission cannot be supported by ions formed in the plasma. Excited atoms play a predominant role in the emission mechanism. Excited atoms generated in the plasma diffuse to the cathode surface. If the work function of the cathode is higher than the difference between the ionization potential and the excitation potential of the atom, the excited atom will be ionized due to resonance ionization at the cathode surface. Because of field emission these ions cause a large number of electrons to be emitted from the cathode in a manner similar to that of the Malter

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[25] E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1945), fourth edition, pp. 22, 23.

[26] C. G. Smith, Phys. Rev. **69**, 96 (1946).

effect. The rapid decrease of electron plasma temperature and population of excited atoms during arc-current interruption offer an explanation for the short extinguishing time of cold-cathode arcs. The similarities between the *D* type of arc and the mercury pool arc suggest that excited atoms play a predominant role in the emission mechanism of low-boiling-point metal arcs.

ACKNOWLEDGMENTS

The author is grateful to Dr. C. G. Smith of Raytheon for advice on operation of the *D*-type arc. Credit is due to Dr. A. D. Sutherland who designed the ultra high-speed camera and performed some of the early studies on the *D*-type arc. The author wishes to thank Mr. F. H. Norman for assistance in performing the experiments.

PHYSICAL REVIEW VOLUME 109, NUMBER 3 FEBRUARY 1, 1958

Cross Quenching of Fluoresence in Organic Solutions*

M. Furst and H. Kallmann
Physics Department, New York University, Washington Square, New York, New York

(Received August 21, 1957)

Concentration quenching is usually considered to occur only between excited and unexcited molecules of the same kind. It is here investigated whether such quenching may also occur between molecules of different structure. Equations are given for testing its occurrence. By using gamma-ray induced fluorescence of solutions containing a combination of two solutes, it is found that concentration quenching occurs between molecules of different structure if their energy levels are close to each other.

I. INTRODUCTION

The fluorescence output under light or high-energy excitation of a single solute solution measured as a function of solute concentration first increases and eventually decreases with increasing concentration at large enough concentrations; this decrease is brought about by concentration (or self) quenching.[1–3] The answer to the question of which elementary process is primarily responsible for this quenching is not yet definitely known although many mechanisms have been proposed. All of these mechanisms have the common assumption that in an encounter between an excited and an unexcited molecule of the same kind a resonance interaction becomes effective which may be attractive or repulsive. This interaction either decreases the emission probability of the molecule (if the lowest state of the two molecules together is less radiative) or it may increase the quenching probability (by bringing the respective molecules closer to each other). Which of these processes is the more important has not yet been ascertained, but in any case it is generally assumed that such a quenching process occurs only between molecules of the same kind. There is the question of whether only identical molecules give rise to the concentration quenching interaction. Does this interaction occur, for example, with molecules which differ from each other only in the position of various groups within a molecule? It is noteworthy in this respect that compounds having related structures and only slight differences in absorption and emission spectra may have large differences in self-quenching, e.g., anthracene and 9,10-diphenylanthracene. The concentration quenching of the latter is about 30 times less than the former. Compounds like anthracene and 2-methylanthracene, on the other hand, exhibit a similar amount of concentration quenching.

It might be expected that concentration quenching and lifetimes of the molecules in solution are correlated, if one conjectures for instance that this quenching is brought about by a resonance interaction proportional to the emission probability per unit time. This probability is proportional to the area under the extinction coefficient curve (as a function of wavelength) in the wavelength region corresponding to the lowest excited electronic energy state; this is proportional to the transition dipole moment responsible for the resonance interaction. Another possibility, just the reverse of the previous, is that concentration quenching is inversely related to the lifetime of the molecule since longer lived molecules have a greater chance for quenching encounters. Neither surmise agrees with experimental evidence obtained from a large number of substances investigated in this laboratory. Consider again, for example, anthracene and 9,10-diphenylanthracene. Anthracene in solution possesses one of the shortest lifetimes but also very large concentration quenching and 9,10-diphenylanthracene has a long lifetime and small concentration quenching. Thus the reasons for large differences in concentration quenching have not yet been determined. There is, however, one result which is consistently found in experiments: it is the decrease of concentration quenching when the mole-

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* This work was supported by the Signal Corps Engineering Laboratories, Evans Signal Laboratory, Belmar, New Jersey.

[1] Peter Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949); also contains an extensive bibliography.

[2] H. Kallmann and M. Furst, Phys. Rev. **79**, 857 (1950).

[3] M. Furst and H. Kallmann, Phys. Rev. **85**, 816 (1952).

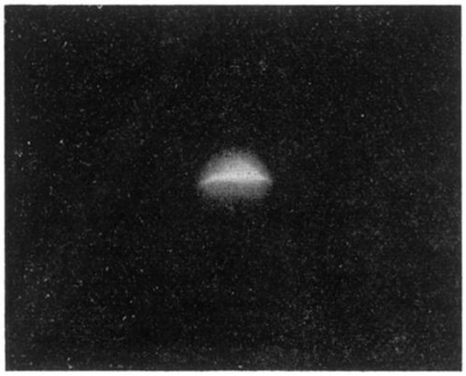


FIG. 7. Photograph of the cathode surface of the *D* type of arc taken with the camera inclined about 30° from the horizontal axis. The bright curved line is the outline of the cathode surface with some of the bright discharge column visible above. Exposure time = 1000 microseconds.

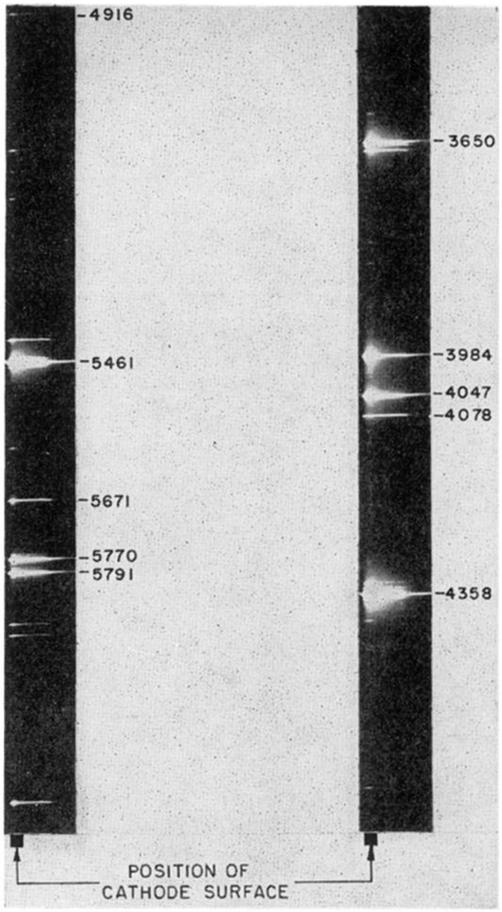
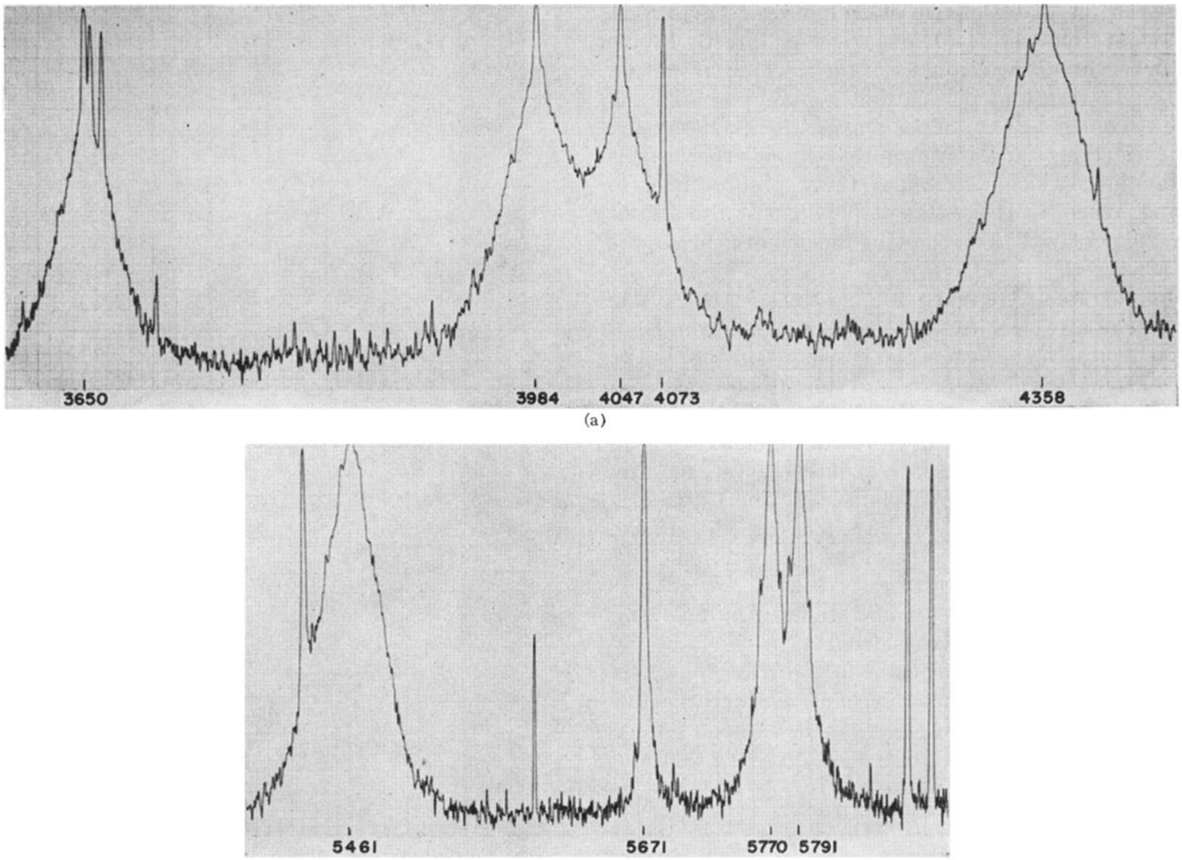


FIG. 8. Spectrum of the *D* type of arc.



(a)

(b)

FIG. 9. Densitometer trace of Fig. 8.