Field Electron Emission from Liquid Mercury

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Field emission from liquid mercury has been investigated by applying an impulsive potential of approximately 10^{-6} sec. duration between a spherical steel anode and a plane mercury cathode. The field just necessary to produce breakdown gave a measure of the field necessary to produce emission because rotating mirror photographs showed that the field emission from the cathode initiated the discharge. The liquid mercury cathode was cooled to a few degrees above its freezing point and the mercury vapor pressure still further reduced by solid CO_2 traps. The mercury could be distilled repeatedly in vacuo and the surface of the cathode changed by "overflowing." The electric field necessary to produce sufficient field emission to start the discharge depended upon the purity of the mercury surface. It varied from 3.5×10^5 volts per cm for impure mercury to 1.8×10^6 volts per cm for mercury that had been repeatedly distilled in vacuo.

THE fact that electrons can be pulled out of solid metals by electric fields of sufficient intensity has been definitely established by many different investigators.[1, 2, 3] A theory of this phenomenon has also been developed[4, 5] which it is claimed[6] is in reasonable agreement with experiment. However, any quantitative comparison of theory with experiment is usually complicated not only by the trouble of getting a uniformly clean pure metal surface but also by the difficulty of determining the value of the electric field at the surface of the metal. This uncertainty in the determination of the electric field at the surface of the metal, arises from the inherent roughness of the solid metal surface, i.e., the electric field at the point of a small projection may be many times that computed for a smooth plane. Therefore, it seemed worth while to attempt a study[7] of the field electron emission from liquid mercury which could not only be purified by repeated distillation in vacuo but also should probably be comparatively free of inherent surface roughness. A study of the field emission from liquid mercury also is of considerable interest in connection with an understanding of the mercury arc, since it is usually believed to be an important factor in maintaining the requisite electron current from the cathode of the arc.[8, 9] In addition to the above, a knowledge of the field necessary to produce appreciable field emission from mercury might prove of value in connection with the design of discharge tubes to withstand high impulsive potentials.

The usual method of studying field electron currents in which a steady potential is applied to the electrodes in vacuo and the resulting current measured by a galvanometer or electrometer obviously cannot be used when one of the electrodes is mercury. The mechanical forces arising from the electric field (0.11 to 11 atm. for fields of 5×10^5 to 5×10^6 volts per cm) will cause the liquid mercury surface to be completely distorted. Therefore, it is necessary to adopt an experimental method in which the electric field is applied and removed from the mercury surface in such a short time that the resulting forces cannot appreciably distort the mercury surface.

It has been definitely shown that if a high impulsive potential is applied across two plane or spherical electrodes in vacuo the resulting dis-

[1] Wood, Phys. Rev. **5**, 1 (1897).

[2] Millikan and Eyring, Phys. Rev. **27**, 51 (1926); **31**, 900 (1928). Millikan and Lauritsen, Proc. Nat. Acad. Sci. **13**, 45 (1928); Phys. Rev. **33**, 598 (1929).

[3] See Compton and Langmuir, Rev. Mod. Phys. **2**, 121 (1930).

[4] Fowler and Nordheim, Proc. Roy. Soc. **A119**, 173 (1928).

[5] Oppenheimer, Phys. Rev. **31**, 66 (1928).

[6] Stern, Gossling and Fowler, Proc. Roy. Soc. **A124**, 699 (1929).

[7] Beams, Phys. Rev. **43**, 781A (1933).

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

[9] Compton, Phys. Rev. **37**, 1077 (1931); Compton and Lamar, Phys. Rev. **37**, 1069 (1931).

charge is initiated by the field electron emission from the cathode.[10, 11] The value of the field required to produce sufficient emission to start the discharge varies for different cathode materials, their purity and their previous treatment but for tungsten is of the order of magnitude of 5×10^5 volts per cm.

Fig. 1a shows a photograph of the light from the beginning of an impulsive discharge between tungsten electrodes in a vacuum after reflection in

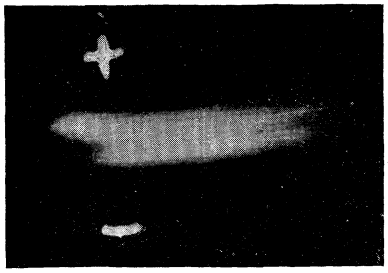


FIG. 1a. Photograph of the beginning of a discharge between two fifty mil tungsten wires in a vacuum. The photograph is magnified seven times. The time between the appearance of the luminosity at anode and cathode in this picture was about 1.5×10^{-7} sec.

a rapidly rotating mirror.[12] Since the image was moving across the photographic plate in a direction perpendicular to a line through the electrodes, it will be observed that the anode becomes luminous before the cathode. This is in accord with the work of Hull and Snoddy who concluded that when the field reaches a certain magnitude the electrons are pulled out of the cold cathode, fall through the high potential difference between the electrodes and bombard the anode. As a result the anode is heated until sufficient vaporization takes place to start the discharge.[11] Fig. 1b shows a similar rotating mirror photograph of an impulsive discharge between a steel ball anode and a liquid mercury cathode. It will be observed that the luminosity starts at the steel anode indicating that the discharge is initiated by the field current from the mercury cathode which heats the steel anode by bombardment and thus initiates the discharge.

[10] Hull and Burger, Phys. Rev. **21**, 1121A (1928).

[11] Snoddy, Phys. Rev. **37**, 1678A (1931).

[12] See Beams, Phys. Rev. **35**, 24 (1930): R. S. I. **1**, 667 (1930) for general method.

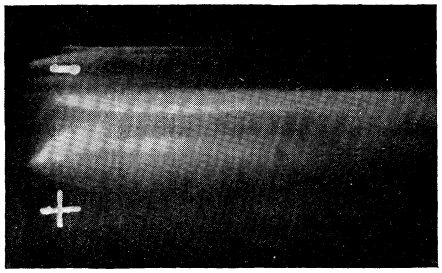


FIG. 1b. Photograph of the beginning of a discharge between a steel spherical anode and a liquid mercury cathode in a vacuum. The time between the appearance of the luminosity at anode and cathode in this picture was about 2×10^{-7} sec. However, this time as well as that recorded in Fig. 1a depends upon a number of factors such as the electrode spacing, power, etc. The faint streak of light above the cathode is due to stray reflected light.

Fig. 2 shows a schematic diagram of the apparatus. The condenser C is charged until the spark gap G breaks down. This applies a potential across the resistance R_1 and to the steel sphere A until a discharge takes place between A and B. The discharge between A and B in turn lights the sensitive neon tube. The potential source was a static machine for the lower potentials and a high potential transformer, in the primary of which a direct current was mechanically broken, for the higher potentials. The spark gap G consisted of two 10 cm brass spheres. The cathode of G was irradiated with ultraviolet light from a quartz mercury arc to reduce time lag effects. The electrolytic resistance R_1 prevented oscillations and was usually adjusted to give a time constant of 1.2×10^{-6} sec. The 2 cm steel spherical anode was mounted on a steel rod about 0.25 mm

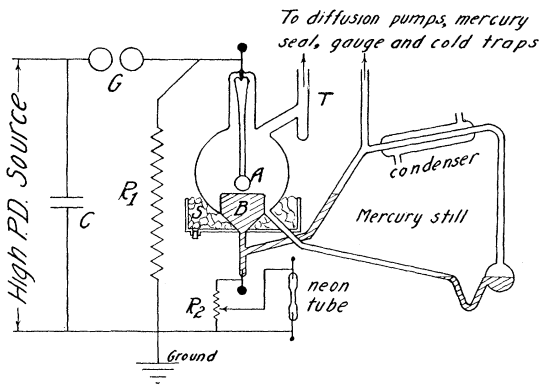


FIG. 2. Diagram of apparatus.

above the maximum height the mercury in B could attain without pouring over the side. It was necessary to avoid violent disturbances of the mercury surface because when the steel sphere and mercury were even reasonably clean the mercury "wetted" the sphere and could be removed only by heating. The electrolytic resistance R_2 prevented violent oscillations in the tube. The neon tube was so arranged that it lighted only when current passed from A to B. It also served as a sensitive means of obtaining the polarity of the discharge. The glass walls of the inner tube containing the mercury B were always electrically shielded from A by the projection of the mercury above the edges of the tube. A freezing mixture of salt and ice S cooled the liquid mercury pool while the trap T, surrounded by solid CO_2, served to reduce the vapor pressure of the mercury in the tube. The surface of B was changed by overflowing and its height regulated by operating the mercury still. A sticking vacuum was always maintained by the mercury diffusion pumps. The mercury was distilled by the Hulett[13] method before being introduced into the clean still. Also the glass tube containing A and B and the traps were baked for 10 hours at 450°C before the mercury was distilled in. The potentials were measured by the width of G. Effects of possible electrical reflections at A were investigated and found to be inappreciable. Distances between A and B were measured by a travelling microscope and the field at B computed by the usual formulas.[14] Care was taken to shield the mercury cathode B from light that might pass through the Pyrex glass, and produce a photoelectric effect on the cathode. Mechanical vibrations of the tube containing B which would cause ripples on the mercury surface were eliminated as far as possible by careful mounting of the tube and by checking the observations late at night, with all pumps, stills, etc., stopped.

When the mercury was first distilled into the tube B, the field necessary to initiate the discharge was about 6.5×10^5 volts per cm. However, as the mercury was repeatedly distilled the field required to initiate the discharge increased at first at the rate of about 10^5 volts per cm per distillation but later much slower until fields of 1.8×10^6 volts per cm were required to start the discharge. Dry nitrogen or hydrogen at about 10 mm pressure when allowed to come in contact with the mercury cathode for a few minutes and then pumped out for an hour seemed to have no appreciable effect on the discharge potential. However, water vapor in sufficient amount or impurities such as grease vapors lowered the discharge potential markedly. Fields of 3.5×10^5 volts per cm were found to initiate the discharge with a cathode containing impurities. In all cases the value of the field necessary to initiate the discharge was critical, i.e., a few percent change in the field caused a change from no discharge to a violent discharge. According to the theory of Fowler and Nordheim[6]

$$I=6.2\times10^{-6}\frac{\mu^{\frac{1}{2}}}{(\mu+w)w^{\frac{1}{2}}}F^2e^{-6.8\times10^7w^{\frac{3}{2}}/F},$$

where I is the field current in amperes per cm^2, μ is a parameter, which they take as 5, w is the thermionic work function in electron volts, and F is the field strength at the surface of the metal in volts per cm. The thermionic work function for liquid mercury has not been experimentally determined but its practical equivalent, the photoelectric work function has been measured many times and found to be 4.53 electron volts for clean mercury.[15] Substituting then the value 1.8×10^6 volts per cm for F, which is the value of the field at the surface of the mercury cathode if it was a perfectly smooth plane, I is of the order of magnitude of 10^{-160} which is considerably less than one electron per sec. and could not possibly start a discharge. From the rate at which heat is conducted away from the anode one can roughly estimate the power and hence the value of I required to start a discharge in 10^{-6} sec. The minimum value of I in this case comes out around one ampere per cm^2. Therefore, in order to account for the discharge field observed, it is necessary to assume either that there exist sharp points on the mercury surface where the field would be increased by a factor of almost 18, that the effective

[13] Hulett and Minchin, Phys. Rev. **21**, 388 (1905).

[14] Peek, *Dielectric Phenomena in High Voltage Engineering*, 3rd edition, Chapter 2 (1929).

[15] See Hughes and DuBridge, *Photoelectric Phenomena*, p. 75.

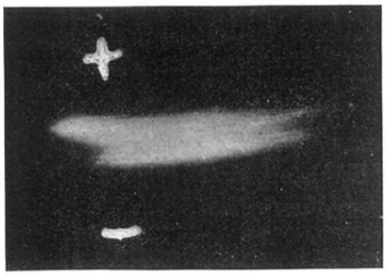
work function varied over large ranges (the maximum value would have to be less than a volt) or that both factors were operating together. The observed increase in the value of the field required to produce a discharge with purification of the mercury surface, indicates that the work function of the surface varied over a considerable range. However, it is not likely that the work function alone could account for the large divergence between formula and experiment even though the assumption is made that the cathode might contain small "patches" with widely different work functions. On the other hand, as far as the writer could find, the exact submicroscopic structure of a liquid mercury surface is not definitely known. X-rays scattered from liquid mercury indicate that "quasi-crystals" may exist in the liquid[16] but since these are so loosely bound, ridges in the surface should not necessarily exist. Very small dust particles were possibly present to some extent in the vacuum system although care was taken to keep the mercury as free from them as possible. The constant breakdown potential observed would require the dust particles, if conducting, all to be of approximately the same dimensions and of the same material if they were causing the breakdown. The distortion of the mercury surface by the mechanical forces arising from the electric field (less than 2 atm.) could not produce points on the surface because in the first place the distortion in 10^{-6} sec. is very small and in the second place it is, by comparison, uniformly distributed and hence could not produce points. Of course if points already existed on the surface the field would increase their height. Mercury droplets should not be pulled out of the surface by the field in 10^{-6} sec. because the internal pressure or cohesive force has been experimentally found to be over 5 atm. while the theoretical value is 13,000 atm.[17] Also the effect of the distortion of the mercury surface by the field was experimentally tested by varying the time of application of the field by a factor of 2, without change of breakdown potential. The natural statistical fluctuations in the surface of the mercury cause a certain roughening of the surface but probably not enough to account for the results observed. Ripples, if present, might account for the results, but as mentioned previously these were eliminated as far as possible. Also they could not be observed by an optical arrangement having a magnification of about thirty. It should also be noted that although the temperature of the mercury was always below 0°C there was still a large number of atoms leaving and entering the mercury surface per second, which would give rise to roughnesses of molecular dimension. In view of our lack of knowledge of the submicroscopic structure of a mercury surface one cannot justly compare the theory with the experimental results obtained above. As a matter of fact, if one could be certain of the direct applicability of the theory valuable information of the submicroscopic structure of the mercury surface could be obtained. The remarkable success of the theory in explaining so many of the experimental results obtained by different investigators with solid metal cathodes indicates that the formula is not far wrong, although it seems that there might be some question as to whether or not the "sharp" potential barriers used in the theory are more than rough approximations to their true shape. It is hoped that the measurement of both the photoelectric threshold (and hence the work function of the surface) and the field necessary to initiate breakdown of the same mercury surface, now being undertaken in this laboratory, may help to straighten out some of the uncertainties.

The experimental results reported above support the field emission theory of Langmuir and Compton for the origin of at least part of the large electron current from the cathode of the mercury arc. Lamar and Compton have shown that in the neighborhood of the cathode of a mercury arc the field is at least 5.7×10^4 volts per cm, which as they point out may possibly give fields of millions of volts per cm at points in the cathode spot produced by the violent agitation. It is likely that the mercury in the arc, although distilled with care, contains sufficient impurities to give enough field emission, with fields of less than 10^6 volts per cm to account for the electron current observed near the cathode of the arc. If it were possible to keep the mercury in an arc really clean, which might be very difficult because of

[16] Debye and Menke, Phys. Zeits. 31, 797 (1930).
[17] Int. Crit. Tables, Vol. 4, p. 19.

impurities liberated by ions and excited atoms from the walls, etc., observations such as those of Lamar and Compton of the characteristics of the arc should perhaps show changes, if field emission is an important factor.

It is a pleasure to record my indebtedness to Mr. James A. Chiles, of this laboratory, who not only kindly obtained the picture 1a but loaned the rotating mirror apparatus with which 1b was secured. Also I am very grateful to Dr. L. B. Snoddy and Mr. F. T. Holmes for the privilege of discussing this paper with them.



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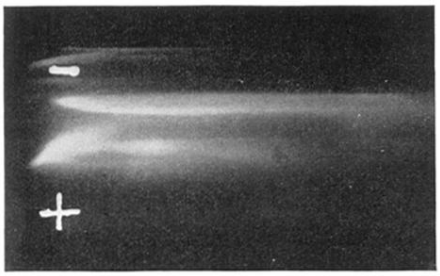

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