

## The Rate of Vaporization of Mercury from an Anchored Cathode Spot<sup>1</sup>

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Two major difficulties which interfere with the measurement of the vaporization of mercury at a free cathode spot are the spray and the normal evaporation from the free surface. By anchoring the spot the spray has been eliminated, and by a specially designed, water-cooled cathode structure the free surface has been limited to small areas of controllable size. By means of a calibrated feed mechanism, mercury was fed to the cathode as fast as it vaporized. Measurements were made over a range of arc current,

cooling water temperature, and exposed area. The rate of vaporization (g/coulomb) increased with arc current, temperature, and exposed area, all due to increased normal evaporation. The rate may also increase with arc current, because of cumulative effects within the spot itself. Extrapolated to zero arc current the rate was found to be approximately  $2.5 \times 10^{-4}$  g/coulomb. This lies within the limits set by von Issendorf. It means that eight elementary charges pass through the arc for every atom evaporated.

THE determination of the rate of vaporization of Hg at the cathode spot of a Hg pool cathode is of considerable technical as well as scientific interest. Several attempts have been made to measure this quantity,<sup>2-4</sup> but the inherent difficulties have made the results inconclusive at best.

It is easily observed that the spot on a Hg surface throws up a spray of droplets whose diameters range from about 0.2 mm down. These constitute the first obstacle to a determination of the vaporization rate, because there is no way of separating the mercury transferred from the pool in this way from that transferred by evaporation. No arrangement of baffles can be devised to do this, for the baffles would either cause vaporization of droplets striking them, thus adding an unknown amount to the vapor, or else they would condense vapor from the stream passing by. It is impossible to control their temperature so that neither occurs.

Guntherschulze made no attempt to separate the spray from the vapor in his pioneer determination. That explains his high result of  $22 \times 10^{-4}$  g/coulomb. Von Issendorf recognized the difficulty and tried to separate the two by dividing his arc tube into two sections, in the first of which the spray collected, in the second of which the vapor condensed. Further, he varied the wall temperature of the first section.

Even so he was able only to set rather wide limits for the true vaporization, namely  $-3 \times 10^{-4}$  and  $+13 \times 10^{-4}$  g/coulomb. Finally, Kobel's arrangement of a small pool at the bottom of a narrow, cooled tungsten funnel assured that little, if any, of the spray would escape, but also must have resulted in the condensation of an appreciable fraction of the vapor itself. His value of  $0.17 \times 10^{-4}$  g/coulomb is certainly low.

A second difficulty lies in the normal evaporation from the exposed surface which, though not exposed at any given instant to the cathode spot mechanisms, is heated by the momentary passages of the spot over it and by the continual flow of energy from the arc stream to it. Because of this factor von Issendorf minimized the area of his pool, but it still was about 4 cm<sup>2</sup> in extent. The low thermal conductivity of the Hg prevents the easy escape of this energy by conduction. In fact rough calculations indicate that in some practical cathode pool constructions the loss of heat by vaporization is comparable with that lost by conduction.

The anchored cathode spot offered an escape from both difficulties, for it gives no spray, and, since the spot is confined to an extremely small area, the exposed Hg surface can be made very small. Whether or not the anchoring of the spot alters the vaporization from it is a question which can be raised but which it is hardly worth while to attempt to answer, as long as there is no adequate theory of the cathode spot, or as long as the rate of vaporization, force, or current density at the free spot cannot be satisfactorily

<sup>1</sup>The subject matter of this paper was reported at the Washington Meeting of the American Physical Society, April 29, 1938, Phys. Rev. **53**, 936 (1938).

<sup>2</sup>Guntherschulze, Zeits. f. Physik **11**, 74 (1922).

<sup>3</sup>J. von Issendorf, Physik. Zeits. **29**, 857 (1928).

<sup>4</sup>E. Kobel, Phys. Rev. **36**, 1636 (1930).

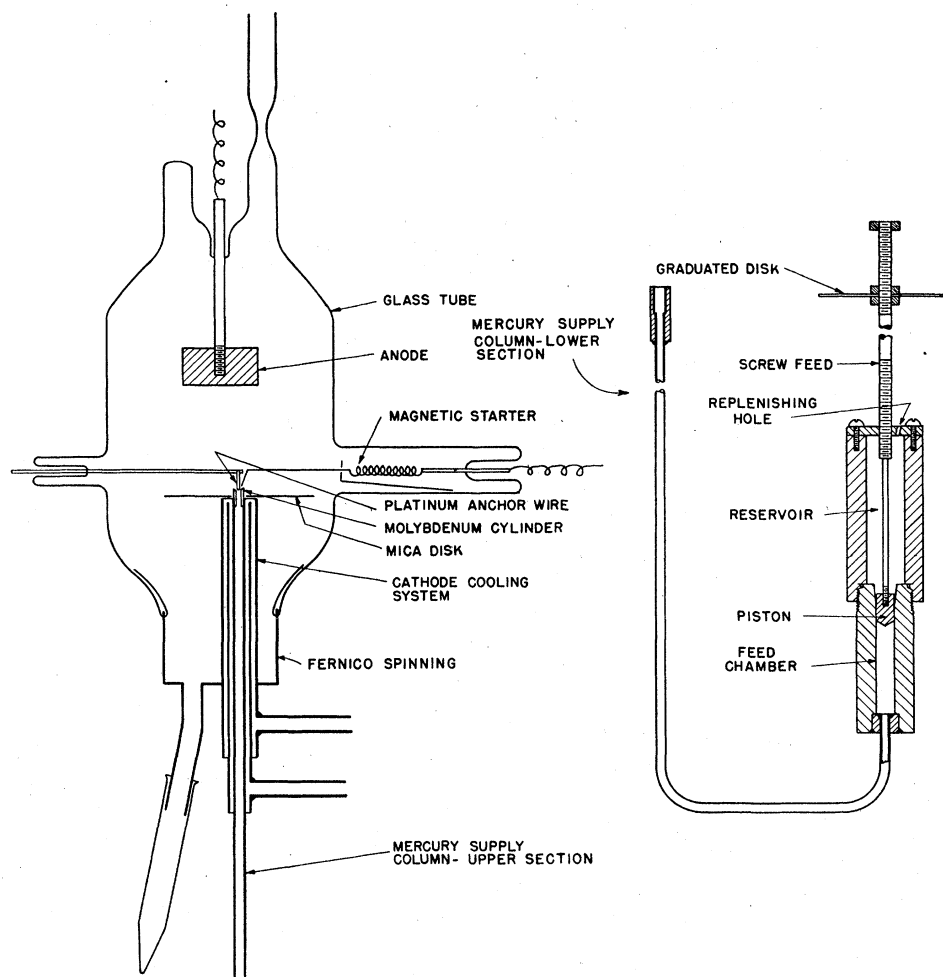


FIG. 1. Arc tube and mercury feed system.

determined. At least, the rate of vaporization from an anchored spot can help in building the theory of the fixed spot, which, in turn, must be the same in its essentials as for a free spot.

The experimental discharge tube and mercury feed system used in the present experiments are shown in Fig. 1. The central feature of the tube is the cathode structure which is shown in detail in Fig. 2. It consists of a Mo cylinder, drilled axially for flow of mercury to the cathode surface, welded to the upper end of the steel mercury feed tube, and arranged to be in good thermal contact with the cathode cooling system. The mica disk was intended to prevent the cathode spot from going to the steel of this system, but despite the shielding which it furnished, the spot

would jump to the mercury accumulated on the floor of the fernico spinning, if the mercury at the tip of the cathode became exhausted. The top face of the Mo cylinder was tapered slightly instead of being turned off flat, with the idea that the cathode spot would anchor there. With the special conditions of small free surface and restricted mercury flow which existed here, it was found to be impossible to maintain a free spot for the time necessary to induce wetting of the Mo. Accordingly, the design was modified by the introduction of the vertical Pt wire dipping into the cathode Hg, for reasonably clean Pt is wet spontaneously by Hg.

Matched thermometers were placed one at the inlet and the other at the outlet of the cooling

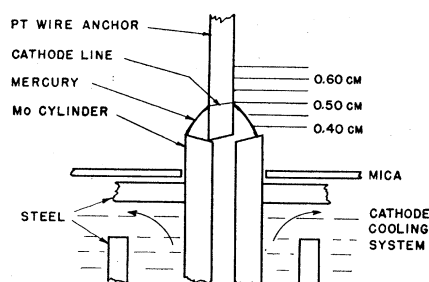


FIG. 2. Detail of cathode structure.

system. The other feature of the apparatus which requires special mention is the arrangement for feeding known quantities of Hg to the cathode spot. It also is shown in Fig. 1. The piston, working in the feed cylinder, controls the supply of Hg to the cathode. The nonwetting of the steel by the mercury made a reasonably close fit, without packing, between piston and cylinder, all that was necessary to assure a positive feed without leakage. The reservoir was designed to permit the replenishment of the Hg in the feed cylinder without the introduction of air between piston and Hg. With the surface of the mercury in the reservoir slightly less than the barometric height below the cathode surface, it was only necessary to raise the piston just out of the feed cylinder to allow fresh Hg to flow down from the reservoir. This arrangement of levels had the further advantage that the pressure tending to force Hg past the piston was small.

The height of the piston was regulated by a screw furnished with a disk graduated in degrees. As the piston diameter was 0.635 cm and the screw pitch 0.106 cm, the constant of the feed system was  $1.265 \times 10^{-3}$  g of Hg per degree.

Before the feed mechanism, as illustrated, was joined to the tube, all parts that were to come into contact with Hg were thoroughly washed with alcohol. The part of the feed system which was connected to the tube had been "pickled," but became oxidized in the heating attendant upon the final sealing process in the making of the fernico seal. No difficulty was foreseen as a result, and none appeared. When the two parts of the system were joined, the junction was made tight with de Khotinski cement.

The attempt was made to prevent the trapping of any air in the feed system when the Hg was

introduced, by holding back the Hg in the reservoir with the piston until the tube, barometric column, and feed cylinder had been exhausted, then allowing the Hg to flow in by raising the piston out of its cylinder. This was, apparently, not completely successful, for the first runs made with the tube showed a varying rate of vaporization in the course of a single determination, but this variability disappeared as experimentation proceeded.

The anode had been fired in vacuum before the tube was assembled. In the tube, which was run on the pump, it was heated briefly by induction, but no special precautions were taken to get the tube gas-free, since small residual pressures of a micron or so would not affect the present cathode phenomenon.

A preliminary experiment in a different type of tube had shown an important effect of exposed mercury surface on the rate of vaporization. In order to maintain a constant exposed area during each determination with the present tube, a cathetometer was sighted on the cathode and the cathode line was held at a fixed level within 0.1 to 0.2 mm by manipulating the feed mechanism.

No special provisions were made for cooling the tube surface upon which the Hg condensed, beyond directing an electric fan upon it. Its temperature never rose above 40°C. Hg vapor at the corresponding saturated vapor pressure, condensing on the small exposed cathode surface, would have no appreciable effect on the experimental results.

The rate of vaporization was measured as a function (1) of arc current, (2) of meniscus height, i.e., exposed Hg surface, and (3) of

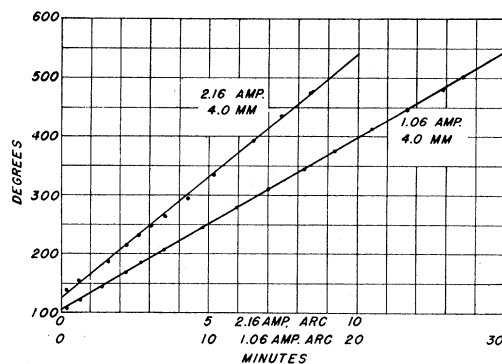


FIG. 3. Plots of experimental data.

cathode cooling water temperature. In making a determination the cooling water temperature was adjusted. The arc was then started and the current was set at the desired value. Finally, the cathode line was set slightly above the chosen height, and at the instant when the line became centered on the cross-hair of the cathetometer a stop watch was started. It was impossible to feed the Hg so evenly that the cathode line remained always at the predetermined height; accordingly, the feeding was manipulated to keep the average height at the desired value. In the early runs, until it became evident that the irregularities in feeding rate which have already been mentioned had disappeared, the elapsed time was noted for approximately every 30° rotation of the feeding head. Later only the total elapsed time was recorded. Fig. 3 shows the results of two runs made in this way. Some deviations from a straight line appear in the measurements at the larger current, but there is little latitude in drawing the best straight line.

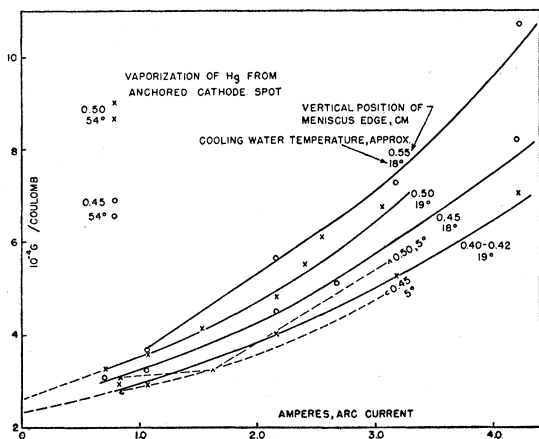


FIG. 4. Rate of vaporization of Hg as a function of arc current.

The results of the measurements are shown in Figs. 4, 5 and 6, which correlate the rates of vaporization with arc current, exposed Hg surface, and cooling water temperature, respectively. It is immediately evident that the vaporization increases significantly as each of these three parameters increases, yet that, extrapolated to zero current or low cooling water temperature, the sequences of values lead to a fairly definite rate of vaporization. From Fig. 4 we find 2.3 – 2.6

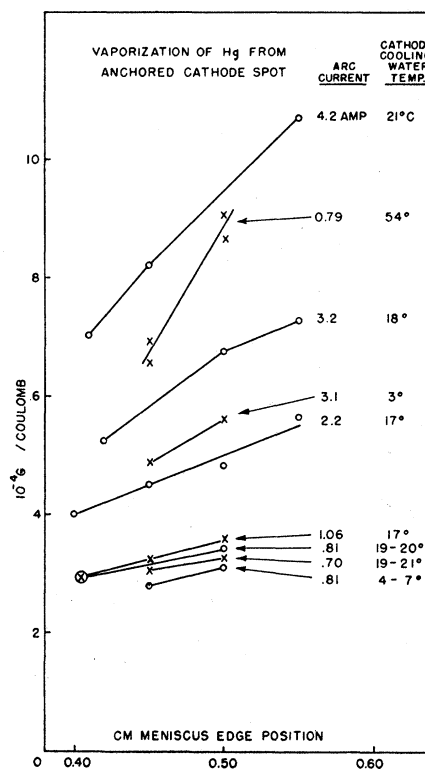


FIG. 5. Rate of vaporization of Hg as a function of exposed Hg area.

$\times 10^{-4}$  g/coulomb, from Fig. 6,  $2.7 - 3.0 \times 10^{-4}$  g/coulomb. It will be noted that these values are an order of magnitude greater than Kobel's, an order of magnitude less than Guntherschulze's, and lie within the range specified by von Issendorf.

Besides the natural evaporation from the free surface, two other factors may contribute to an increase in vaporization rate. The one is an increase from the cathode line itself with increasing current density. This would only become evident as a residual effect after other causes had been considered. The other factor is condensation on the cathode Hg of Hg vaporized at the spot. It is to be expected that this effect will be the greater the more confined the cathode line is by the liquid Hg, that is, the lower the meniscus edge. The consequence would be an increase of vaporization with meniscus height, that is, an effect similar to that of natural evaporation, except that now the "true" rate is more closely approached as the meniscus is raised.

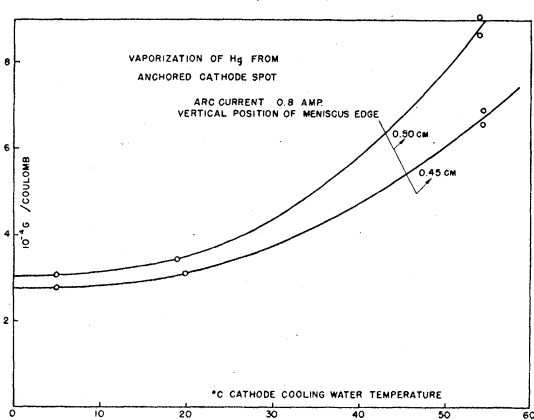


FIG. 6. Rate of vaporization of Hg as a function of cathode cooling water temperature.

We should expect the true evaporation to take place into the hemispherical solid angle above the plane over which the cathode spot is playing. If the liquid Hg cuts off one-half this angle, as it would in the present case, if the meniscus edge lay slightly below 0.4 cm, then only one-half of the vaporized Hg would escape. If the angular opening between anchor and surface is increased to  $135^\circ$ , then 85 percent or more would escape. No increase comparable with this is seen at the low current values where the effect should be looked for uncomplicated by the other factors. We conclude that the effect is small here, although it probably exists.

If we assume that the whole increase in vaporization with meniscus height and current is due to natural evaporation, we can make an estimate of the surface temperature of the cathode mercury for a particular value of current, say, 2.15 amp. Fig. 4 shows a difference of vaporization rate  $\Delta R$  of  $1.6 \times 10^{-4}$  g/coulomb between the 4.1 mm and 5.5 mm meniscus positions. If the free surface be assumed to have the area of the conical surface of the frustum of a cone in the two cases, we find 0.06 cm<sup>2</sup> and 0.13 cm<sup>2</sup>, respectively. If we further suppose the surface temperatures to be the same, we have to calculate the temperature at which Hg vaporizes at the rate

$$\frac{1.6 \times 10^{-4} \times 2.15}{0.13 - 0.06} = 4.9 \times 10^{-3} \text{ g/cm}^2 \text{ sec.}^{-1}.$$

This mass-transport of Hg vapor, expressed in

terms of pressure (assuming 300°K) is, from the kinetic theory relation,  $3.58 \times 10^{-5} p$  (bars), so that

$$p = 137 \text{ bars,}$$

corresponding to saturated Hg vapor at 83°C. This is not an unreasonable temperature in view of the low heat conductivity of Hg.

It is important to note that even the small free surfaces met with here can evaporate as much or more Hg than the cathode spot itself.

Table I shows the results of previous determinations of vaporization rates in vacuum for Cu and Zn. The spread in values between the Easton-Lucas-Creedy, the Tanberg, and the Robertson results cannot be accounted for in terms of gas pressure, for Robertson found only a small effect—and that a decrease—from increasing nitrogen pressure.

The present result for Hg fits well with Robertson's Cu value. This is particularly striking if we compare the net rate at which atoms leave the metal to the rate of transfer of elementary charge. The rate of  $2.5 \times 10^{-4}$  g/coulomb for Hg corresponds to 0.12 atoms/elementary charge. Similarly,  $0.87 \times 10^{-4}$  g/coulomb for Cu gives 0.13 atom/elementary charge. Reasoning rigorously, the Cu value should also be extrapolated to zero current instead of using the 15 amp. value. Since, however, the vapor pressure of the Cu is negligible, it will not contribute to an increase of vaporization with current. Thus, the comparison, as made, fails only to take into account a possible intrinsic increase of vaporization with current for the Cu spot. It is interesting that there is a small number ratio between the elementary charge transfer and the number of atoms which escape without immediate recondensation as either atom or ion. Thus, if the current is carried chiefly

TABLE I. Results of previous determinations of vaporization rates in vacuum for Cu and Zn.

MATERIAL	PRESSURE (MICRONS)	GAS	CURRENT (AMP.)	RATE ( $10^{-4}$ g/COULOMB)	REFERENCE
Cu	40-50	Residual	70-150	0.07	(1)
Zn	40-50	Residual	40	0.1	(1)
Cu	0.2-10	Residual	75	0.13	(1)
Cu	0, extrapolated		11-32	0.15	(2)
			15	0.87	(3)

<sup>1</sup> Easton, Lucas Creedy, Elec. Eng. **53**, 1454 (1934).

<sup>2</sup> Tanberg, Phys. Rev. **35**, 1080 (1930).

<sup>3</sup> R. M. Robertson, Phys. Rev. **53**, 578 (1938).

by electrons, some 8 electrons evaporate for every atom.

Table I makes it apparent that an important factor contributing to the high velocity of the vapor stream which Tanberg calculated is a low value of the rate of evaporation. As I have pointed out,<sup>5</sup> the rate of vaporization for Hg found in the present experiment is consistent with the force on the cathode which has been observed. A potential maximum of about 3 volts above space, i.e., about 13 volts above cathode, in the cathode spot plasma with complete ionization of the vapor there would account for the observed force.

<sup>5</sup> Tonks, Phys. Rev. 50, 226 (1936).

The smallest current maintained by a spot anchored on a tungsten "Schwamm" is given by von Engel and Steenbeck<sup>6</sup> as 50 ma. The smallest currents I have observed from a porous body of Mo saturated with mercury have been in the neighborhood of 0.5 amp. The present result shows that in these cases the vaporization was at the rate of 1.2 and  $12 \times 10^{-5}$  g/sec., respectively. It may be that vaporization rates lower than these would give a density of gas immediately above the cathode spot which is insufficient to establish the electron emission condition.

<sup>6</sup> Von Engel and Steenbeck, *Elektrische Gasentladungen*, Vol. II, p. 263.

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## The Effective Cross Section of Positive Alkali Ions with Respect to Gas Molecules

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The absorption of positive sodium ions with velocities of 40 to 400 equivalent volts has been studied in hydrogen, nitrogen and oxygen. The nature of the collision processes has, in each case, been studied to determine the relative importance of neutralization, retardation or small angle scattering. The mean free paths and effective cross section of the sodium ions with respect to the gas molecules is found to be a function of the pressure of the gas, the velocity of the ion and the nature of the gas-ion combination. The effective cross section of each gas-ion combination

approaches the kinetic theory value at low velocity of the ion while at high velocities it approaches a minimum considerably smaller than the kinetic theory value. At any given velocity over the range studied, the effective cross section of the gas-ion combination increases in the order hydrogen, nitrogen, oxygen. The values for nitrogen and oxygen are essentially, within experimental errors, equal. An improved furnace for the production of positive ions has been developed.

A NUMBER of investigations have been made on the absorption of slow positive ions in gases. The absorption may be due to small angle scattering, retardation or neutralization. The method of investigation generally used has been to bend a beam of positive ions in a magnetic field and measure the rate of absorption of the ions over a fixed length of path. The rate of absorption has been found to be a function of the pressure of the gas, the nature of the gas-ion combination and the speed of the ion. G. P. Thompson<sup>1</sup> found considerable small angle

scattering of  $H^+$  ions in  $H_2$ , He and A. Dempster<sup>2</sup> passed  $H^+$  ions, accelerated between 14 and 1000 volts, into helium. Little, if any, retardation was observed, but considerable scattering of the bundle of protons was found at high pressures. Durbin<sup>3</sup> measured the rate of absorption of  $K^+$  ions in He,  $H_2$ , A,  $N_2$  and  $O_2$ . He found the absorption of the ions to increase with the pressure of the gas and with a decrease of velocity of the ions. In all cases, the mean free path was found to be greater than the kinetic theory mean free path, but it approached the

<sup>1</sup> G. P. Thompson, Phil. Mag. [7] 1, 961 (1926); Phil. Mag. [7] 2, 1076 (1926).

<sup>2</sup> A. J. Dempster, Phil. Mag. [7] 3, 115 (1927).

<sup>3</sup> F. M. Durbin, Phys. Rev. 30, 844 (1927).