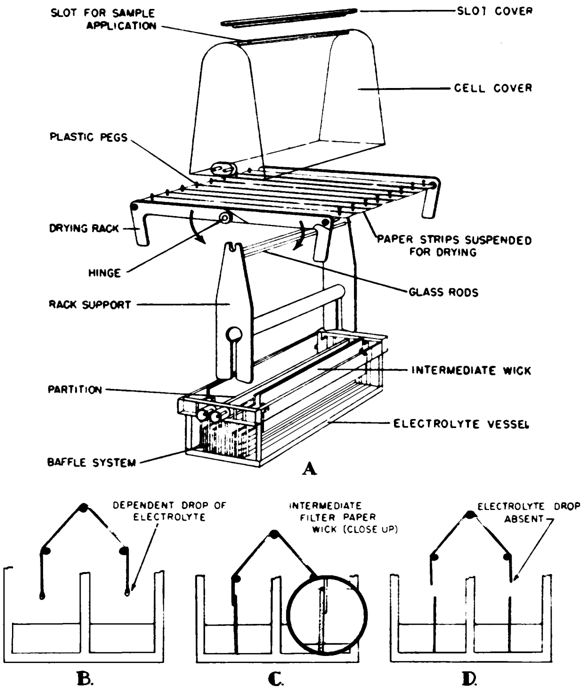

Fig. 2. Hanging-strip paper-electrophoresis cell and rack. (*A*) Cell with parts separated for visualization. (*B*) Formation of dependent drop of electrolyte. (*C, D*) Elimination of drop by intermediate wick.

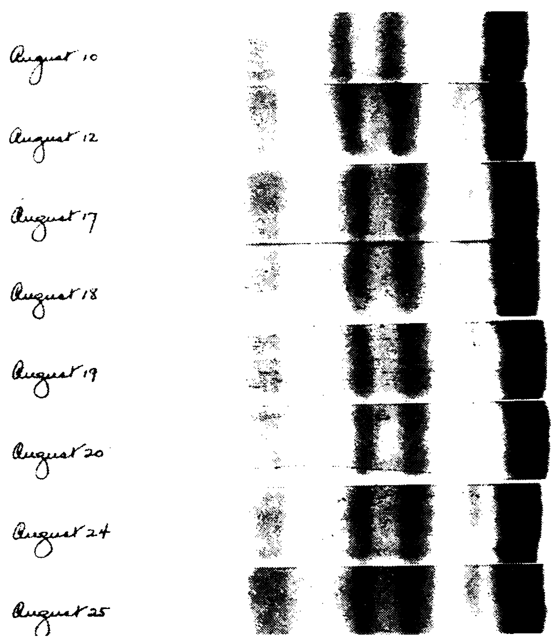

Fig. 3. Reproducibility study. Strips from eight different experiments, performed on the dates indicated, with the cell shown in Fig. 2. The experimental conditions were Whatman No. 3MM filter paper, eight strips 29 by 300 mm, 0.01 ml of serum applied at the apex, barbital buffer pH 8.6, $\mu = 0.075$, 16-hr duration, constant current of 8 ma (for eight strips), and stained with bromphenol blue (*4, 6*).

Under these conditions the strips dry with practically no shift of the resolved zones. This procedure also prevents the formation of apical creases, which are difficult to avoid when any of the heavier papers (for example, Whatman No. 3MM) are dried over an apical rod. Since these creases are reproduced as spikes by most photoelectric scanners, they may obscure the "application artifact" which is caused by the presence of particulate material, traces of fibrinogen, and other substances in the serum that are precipitated or otherwise bound at the origin. The application artifact probably has clinical significance.

Figure 3 illustrates the reproducibility and resolution obtainable with apparatus of this design when Whatman No. 3MM strips, 29 by 300 mm were used. The same serum was studied during eight different experiments over the course of 2 wk.

References and Notes

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1. E. L. Durrum, *Abstracts of Papers, 115th Meeting, American Chemical Society* (1949), p. 22C; *U.S. Army Medical Dept. Field Research Lab. Rept.*, Proj. 6-24-12-06 (18) (1949); *J. Am. Chem. Soc.* **72**, 2943 (1950); *J. Colloid Sci.* **6**, 274 (1951).
2. F. V. Flynn and P. deMayo, *Lancet* **1951, II**, 235; M. Macheboeuf, P. Rebeyrotte, M. Brunerie, *Bull. soc. chim. biol.* **33**, 1543 (1951); T. H. Spaet, *J. Lab. Clin. Med.* **41**, 161 (1953); Ch. Wunderly and B. Cagianut, *Ann. Oculist* **185**, 414 (1952).
3. H. G. Kunkel and A. Tiselius, *J. Gen. Physiol.* **35**, 89 (1951).
4. R. J. Block, E. L. Durrum, G. Zweig, *A Manual of Paper Chromatography and Paper Electrophoresis* (Academic Press, New York, 1955).
5. If support rods are small in diameter and are treated with a silicone antiwetting agent, no meniscus forms at the point of contact between the support rod and the paper during electrophoresis, and no distortion of field or other artifact is detectable.
6. W. P. Jencks, M. R. Jetton, E. L. Durrum, *Biochem. J.*, in press.

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Use of Narrow Holes for Producing Glow-to-Arc Transitions

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When, in experimental apparatus designed to confine the cathode spot on the surface of a mercury pool to a small area (*1*), a pinhole is left in a funnel-shaped glass member joined to the envelope in a ring-seal (*2*), a glow-to-arc transition usually results in an arc passing through the pinhole. These observations are presented as unmistakable evidence that a concentration of current in the positive column of a glow discharge is a condition that favors the establishment of a cathode spot and the resulting transition to the arc. If the hole is in the millimeter-size range, the arc takes the path through it in the majority of cases over a considerable range of gas pressures. In a glow discharge, the current density through a hole of fixed size can be increased by adding appropriately placed conducting extensions to the cathode, and this increases the probability that the arc will be set up through the hole.

The form of the tubes used in this investigation is suggested by Fig. 1. A hole is intentionally left in the wall of the constriction, and its approximate size is measured. With a given geometry, in which the size of the hole is a dominating factor, there is a definite variation with vapor pressure in the ratio of the number of times the arc is initiated within the constriction to the number of times it is formed through the hole in the constricting member. This is shown in Fig. 2, where the ambient temperatures of the experimental tube shown on the X-axis correspond to the vapor pressures shown at the top of the figure. The proportion of the glow-to-arc transitions that take the path through the hole is plotted on the Y-axis.

The sampling procedure is to raise the potential difference between anode and cathode until the arc is established and to record whether or not the arc column passes through the hole. The data plotted in Fig. 2 were obtained by repeating the procedure until 20 events of the same kind had been recorded, and since this did not result in samples of large size, considerable statistical fluctuation associated with the experimental points plotted is to be expected. The first curve, at the lower right-hand side of the figure, corresponds to a hole of approximately circular cross section with a diameter of about 1 mm. This curve shows the characteristic behavior of the phenomenon as the vapor pressure is varied. At low vapor pressure, none of the glow-to-arc transitions takes the path through the hole. The onset of the phenomenon requires sufficient vapor pressure to supply current carriers for the concentration of the current through the hole. At intermediate vapor pressures of about 1 mm, more of the glow-to-arc transitions take the path through the hole than take the direct path down the funnel. As the vapor pressure is raised above 1 mm, the proportion that take the path through the hole decreases. The cause of this decrease has not been

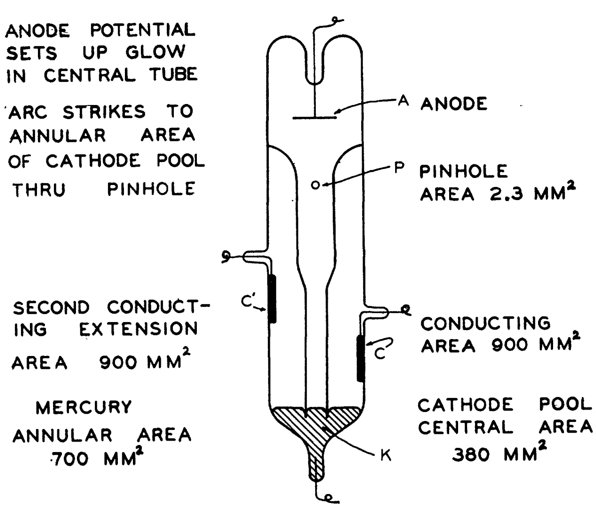

Fig. 1. Experimental tube for the production of glow-to-arc transitions through a pinhole.

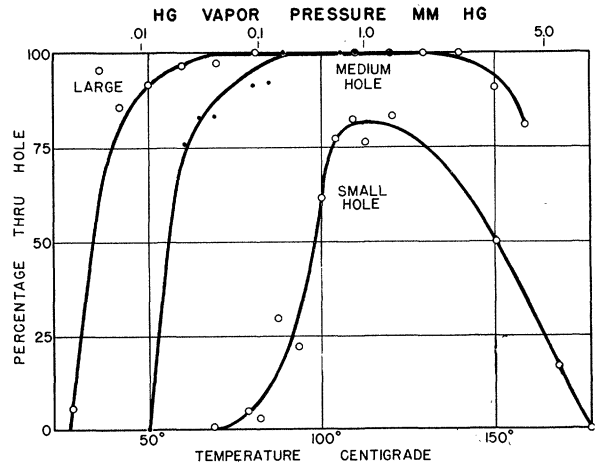

Fig. 2. Statistical distribution indicating the probability of the arc stream passing through holes of various sizes as a function of vapor pressure.

established. It should be mentioned, however, that at pressures in this range, the discharge begins to concentrate in streamers, whether or not there is a constriction anywhere along the path. Also, in this range of pressures, the potential gradient along the column increases; thus, the more direct path would be favored.

If the hole is enlarged, the transitions through the hole occur at lower pressures and also at somewhat higher pressures. The intermediate curve of Fig. 2 was obtained by using a hole of circular form having an approximate diameter of 2.5 mm. In this case only 0.1 mm of vapor pressure is required for the larger share of the transitions to take the path through the hole. There is a considerable range of vapor pressures in which transitions through the hole occur in virtually all the tests.

The curve marked "large" was obtained with a hole in the form of a slit about 1.5 mm wide and 6 mm long. Glow-to-arc transitions through this hole begin at pressures of slightly less than 0.01 mm. There is a relatively wide range of pressures in which glow-to-arc transitions take the path through the hole in virtually all the tests. There is a decrease in the proportion of transitions through the hole at the higher pressures, and further work with different experimental tubes has shown that this trend persists until the arc stream in all tests takes the direct path down the funnel.

The dependence of this phenomenon on pressure has been verified by experiments in which the gas used was air and also in other experiments in which helium was used. The data on tubes containing helium were especially interesting, for the breakdown potentials were very low and the glow-to-arc transitions were very rapid. The length of the arc stream in two such tubes was about 12 in., and the diameter of the hole was about 1.75 mm. At optimum pressure, estimated to be about 0.5 mm, glow in such tubes was set up at about 600-v potential difference, and the transition to the arc took place quickly. In another similar tube containing helium at a pressure of about

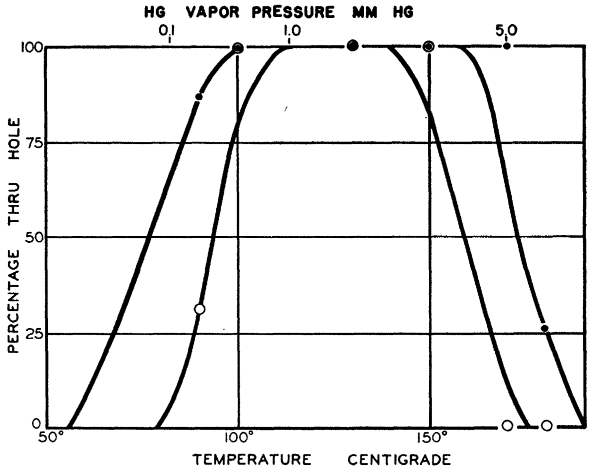

Fig. 3. Increase in the proportion of glow-to-arc transitions through a hole produced by the addition of a 900-mm^2 conducting extension to the cathode. Open circles indicate results obtained without the use of the extension. The small black circles indicate results obtained with one extension connected to the cathode through a 10,000-ohm resistance.

1.5 mm, the breakdown required 1000 v, but the transition was so rapid that the arc appeared to be set up directly.

Although the arc is often established so quickly that no glow appears to precede it, under other conditions the glow is seen to be established with the small portion of the pool within the funnel as a cathode. This area is so small that, with modest currents, an abnormal cathode fall is required for the liberation of the electrons from the cathode. In this case, there is a tendency for the glow to overspread a larger area of the cathode pool in order to reduce the abnormal cathode fall. Ions are present in the vicinity of the pinhole, and they are drawn through it by the potential gradient. A glow is then established in the large, outer portion of the tube. The pool area outside the constriction is sufficiently large that, with the potential difference applied, a relatively large concentration of the current is set up at the hole. Over a considerable range of vapor pressures, this provides the conditions needed to establish the arc along this path.

The efficiency of the process would be expected depend not only on the size of the hole but also on the cathode area outside the funnel. This has been verified by experiments performed with the tube shown in Fig. 1. As the drawing shows, this tube is provided with two conducting areas, C and C', that were made by painting the inside wall of the tube with a platinum alloy. Each of the two areas is provided with a lead-out wire by means of which it may be electrically connected to the cathode K. If this connection is made directly, the cathode spot is most likely to be set up on the platinum alloy, and the conditions in this case differ enough that comparisons with data in which the spot is established somewhere on the mercury pool may not be justified. To avoid such criticism, the platinum alloy areas have been connected to the cathode through a resistance of about 10,000 ohms. This resistance is high enough to prevent the formation of the cathode spot on the platinum alloy, but it is low enough to permit the alloy to serve as additional cathode area for the glow discharge passing through the pinhole.

The results obtained show that the connection of the platinum area to the cathode through the resistance generally increased the ratio of the number of times that the cathode spot was set up on the annular area of the mercury pool to the number of times that it was set up within the funnel. The data obtained are plotted in Fig. 3; the lower curve was obtained without either of the platinum areas, and the upper curve was obtained by using the single platinum alloy area nearest to the cathode pool. It was also verified that the addition of the second patch raised the curve somewhat.

References

1. C. W. Lufcy and P. L. Copeland, *J. Appl. Phys.* **16**, 740 (1945).
2. P. L. Copeland, *Rev. Sci. Instr.* **16**, 154 (1945).

21 February 1955.

Communications

Demonstration of the Basicity of Water in Alcoholic Solutions

Experiments either designed or interpreted as determining the relative basicity of water versus alcohols have given contradictory answers. Hammett (*1*) points out that because charged acids such as ammonium ion have smaller pK_a values in ethanol than in water, one may conclude that the former is the more basic solvent. On the other hand, the same author cites references to colorimetric and acid catalyzed reactions that indicate the reverse. Hine and Hine (*2*), in reviewing the literature on both the relative acidity and basicity of water versus alcohols, also show that these evaluations depend on the system chosen for study.

The simplest way of assessing the relative magnitude of a given property of two substances is through a competitive situation. In studying the solvochromism (*3*) of alcoholic solutions of an indicator composed of propyl gallate and ferric chloride, we observed that the blue color of the chelate was promoted