[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PHOTOCHEMICAL TECHNIQUE. I. A SIMPLE CAPILLARY MERCURY VAPOR LAMP

BY FARRINGTON DANIELS AND LAWRENCE J. HEIDT

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This lamp[1] was designed to meet the demand for an intense source of ultraviolet light for photochemical investigations and particularly for illuminating the slit of a monochromator. Mercury lamps and other sources of ultraviolet light have been reviewed.[2,3] Forbes and his co-workers[4,5] have developed an effective capillary mercury vapor lamp and have studied carefully its characteristics. The lamp described here is less permanent and it must be water cooled, but it is simpler and cheaper. One can afford to run it at a great overload, thus giving a higher intensity.

Description

The simplified lamp, shown in Fig. 1, is made of quartz tubing[6] with an inside diameter of 1 to 2 mm. and a wall 0.7 to 1 mm. in thickness. Tubes of larger diameter may be used. A tube about 12 cm. long is provided with two bulbs, A and B, blown out in the gas–oxygen flame with a space of 5 to 30 mm. between them when operated on d. c. line voltages of 50 to 600 volts, respectively. The bulbs are blown as thin as is consistent with mechanical strength. Their function is to keep the arc localized between A and B. They prevent the arc from extending farther, because the thin walls are cooler and because the larger diameter reduces the current density. The more completely the arc is thus localized the steadier is the lamp. Tungsten electrodes, 0.5 mm. smaller in diameter than the containing tube, are preferable, but nickel or iron (hay wire) may be used.

The upper, positive electrode, E, is set with de Khotinsky cement (shellac and pine tar) flowed into the warmed tube as shown by the cross hatching. The lamp is filled by placing the open end under purified mercury, evacuating and then releasing the vacuum. The lamp is then inverted and the electrode D is sealed in with cement. Silver chloride or other high melting, sealing cements used with bulbs in the earlier models are unnecessary if a rapid stream of cold water is employed. The uppermost

[1] Preliminary descriptions have been given in THIS JOURNAL, **52**, 2151 (1930), and in Daniels, Mathews and Williams "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1929, p. 423.

[2] Ellis and Wells, "The Chemical Action of Ultraviolet Light," Chemical Catalog Co., New York, 1925.

[3] Forbes, *J. Phys. Chem.*, **32**, 485 (1928).

[4] Harrison and Forbes, *J. Opt. Soc. Am.*, **10**, 1 (1925); **11**, 99 (1925); THIS JOURNAL, **47**, 2449 (1925).

[5] Leighton and Forbes, *J. Phys. Chem.*, **30**, 1628 (1926).

[6] Quartz tubing may be purchased from the Hanovia Chemical and Manufacturing Co. of Newark, N. J., from the General Electric Co., Schenectady, N. Y., from the Thermal Syndicate, Brooklyn, N. Y., or from The Quartz Products Manufacturing Co., 69 Tichenor St., Newark, N. J. The cost of tubing for a lamp is less than a dollar.

bulb, C, serves as the expansion chamber into which the mercury is driven when the arc is struck and the space between A and B is filled with incandescent mercury vapor. The size of this bulb and the level of the mercury determine the expansion volume. The ratio of the arc volume to this expansion volume determines the pressure under which the lamp operates. A small expansion volume gives a high pressure and a correspondingly high resistance. When 550 volts are available, the volume can be small, leading to pressures of 2 to 5 atmospheres and giving high-voltage, low-amperage lamps.

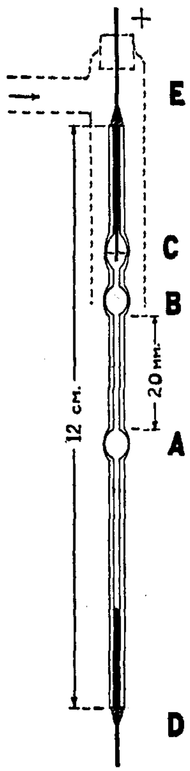

Fig. 1.—Capillary mercury vapor lamp of quartz. Inside diameter, 2 mm. Wall thickness, 0.7 to 1.0 mm.

The protruding electrodes of the lamp are connected with rubber-insulated wires and the bare connections are then insulated by covering with de Khotinsky cement. The wires are connected with a direct current dynamo through an adjustable resistance. A 22-ohm, 5-ampere resistance is sufficient for use on a 110-volt circuit but on a 550-volt circuit several additional resistances are necessary.[7] The resistance of the lamp varies from nearly zero before the arc is struck, to 20 to 500 ohms when operating depending on the expansion volume and on other factors.

Cooling with a large, rapid stream of cold water is absolutely necessary. Without it the seals and the quartz itself are melted. Hard water may be used if the stream is sufficiently rapid; otherwise, the outside of the lamp becomes hot enough to form a deposit.

To start the lamp the mercury is shaken down, the circuit is closed and the mercury thread in the capillary is then separated by playing on it a small Bunsen flame. The instant the arc strikes, water is turned on. The lamps have been started, also, with a small electric heating coil wound around the capillary just above the bulb A.

The protruding end of the upper electrode passes through a rubber stopper which fits into a T-tube of glass 1 cm. in diameter, extending to the bulb B. The tube is shown by dotted lines in Fig. 1. In this way an encircling stream of water is directed down around the lamp to a waste pipe. Best results are obtained by mounting the lamp in a copper tank provided with a quartz window and drain and overflow tubes, 3 cm. or more in diameter. A brass frame soldered to the tank and a similar frame screwed against it hold the quartz window in place with rubber gaskets. The tank is emptied with the drain, and after the lamp is started the tank is allowed to fill, thus completely immersing the lamp.

Caution.—There is danger from a lamp bursting although the stream of water and particularly the tank mounting minimizes this danger. Special care is necessary to avoid ultraviolet burns.

The lamps operate well on 110 volts and 3 to 5 amperes. A 550-volt source permits greater intensity. If the lamps fail to start properly it may be necessary to (a) increase the voltage, (b) decrease the mercury level, thus giving a greater expansion chamber, a lower pressure and consequently a lower resistance and higher current, or (c) change the diameter of the capillary. If the current increases seriously while the lamp is operating one may suspect a leak at the seals. More effective cooling is then necessary. An inexpensive ammeter should be included in the circuit.

[7] "Glow" resistances, for radiant heaters, which screw into an electric light socket, are convenient and cheap.

Tests

Each lamp has its own characteristics but in general the intensity of radiation, E_λ, of a particular wave length is nearly proportional to the wattage, W, of the lamp. The formula $E_\lambda = aW$, is a rough approximation to the average behavior between 500 and 1500 watts. When E_λ is determined as ergs per second falling on a sq. mm. of a thermopile after passing through a large monochromator and W is the product of the amperage and the voltage drop across the lamp, the constant a has the following values: 1 for 265 and 280 mμ; 5 for 302 mμ; 7 for 313 mμ; 2 for 334 mμ; from 12 to 20 for 365 mμ; from 4 to 8 for 404 mμ; and from 6 to 12 for 436 mμ. The short ultraviolet lines give about the same intensity per watt regardless of the voltage, but the 404 and 436 mμ lines are more intense at high voltages. The larger values of a correspond roughly to 500 volts and the smaller values to 100 volts. The distribution of energy will be shown more fully in Fig. 3 of the following article. The lines below 265 mμ are weak and there is extensive reversal of the line at 253.6 mμ.

Plotting amperes through the arc as ordinates against voltage across the arc as abscissas, the curve passes through a maximum. However, plotting resistance across the arc as ordinates against voltage the curve is linear.

Aging varies. Perhaps twenty-four hours of operation is a common life. When operating below 500 watts, a lamp may last much longer. After heavy usage, a white deposit forms on the inside of the lamp which shows, under the microscope, a distorted honeycomb structure. For the internal 0.05 mm., however, these minute cracks are fused together, showing that the effective temperature of the arc is above the melting point of quartz (1700°). The outside of the tube 0.7 to 1 mm. away from the arc is at about 20° and the cracks may be due to this enormous temperature gradient, or possibly to crystallization. The white region of cracks does not cause a large reduction in intensity but a few cracks spread out and eventually one of them causes the lamp to break. Lamps with thick walls break much sooner than those with thin walls.

The efficiency of the lamps was tested also with 100 cc. of a solution, 0.8 molar in oxalic acid and 0.05 molar in uranyl sulfate, placed in a hollow, cylindrical, quartz cell completely surrounding the lamp. Using a lamp at 570 volts and 2.7 amperes, 6.16 g. of oxalic acid was decomposed in eight minutes, corresponding to 0.77 g. per minute and to 0.24 mole per kilowatt hour. Taking the quantum efficiency of this reaction as 0.6 molecule per quantum[8] the photochemical action consumed 0.4 einstein (1 einstein = 6.06×10^{23} quanta) per kilowatt hour of energy supplied to the lamp. Similar results were obtained with a stream of solution passing through a concentric, cylindrical cell only 5 cc. in capacity. In experiments with rectangular quartz cells at a distance of about 10 cm. these

[8] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).

capillary lamps gave over one hundred times as much photochemical action as a commercial lamp.

The chief reason for the high intensity (per sq. mm. of lamp surface) is the high concentration of energy. The volume of the arc in the capillary lamp is approximately 0.05 cc. as against 20 cc. in a commercial lamp. Although the volume of a commercial lamp is 400 times as great, the total input of energy is less. The dimensions of the capillary lamp are such that a much greater fraction of the radiation emitted by the lamp can be brought to the slit of a monochromator or passed into a reaction cell of ordinary dimensions.

The authors are pleased to acknowledge the help contributed by Mr. Glenn Damon and Mr. Harrison Holmes to the development of the lamp described here.

Summary

An inexpensive quartz mercury vapor lamp of high intensity has been described and tested.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PHOTOCHEMICAL TECHNIQUE. II. CONSTRUCTION AND TESTS OF A QUARTZ MONOCHROMATOR[1]

BY LAWRENCE J. HEIDT AND FARRINGTON DANIELS

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Monochromatic radiation of measured intensity is necessary for the quantitative study of photochemical reactions. Separation of the different wave lengths by refraction in a monochromator offers the most effective method for obtaining this radiation but the energy flux available at any one wave length is extremely low on account of losses due to reflection, absorption, slit dimensions, etc. To minimize this handicap a more intense source of light was developed.[2] Further efforts to increase the radiation intensity by using a monochromator of large dimensions and favorable optical conditions are described in the present communication.

The subject of monochromators and of photochemical apparatus has been reviewed in detail by G. S. Forbes.[3] The dimensions and material of the prism and lenses used in the present investigation are approximately those described by Marshall and Knudson.[4] The purpose of

[1] Complete details of the dimensions and calculations may be obtained from the Ph.D. Thesis (June, 1930) of the first author, which is on file in the Library of the University of Wisconsin.

[2] Daniels and Heidt, THIS JOURNAL, **54**, 2381 (1932).

[3] Forbes, *J. Phys. Chem.*, **32**, 482 (1928).

[4] Marshall and Knudson, *ibid.*, **52**, 2304 (1930).