oxide in hydrochloric acid with the measurements for the corresponding quantity for calcite that were presented in the preceding paper. On the basis of this value a free-energy equation for the reaction, $CaCO_3 = CaO + CO_2$, has been derived, which represents the dissociation-pressure measurements within limits of error and yields a value for the entropy of carbon dioxide, which is in good agreement with values obtained from other sources.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY AND THE JEFFERSON PHYSICAL LABORATORY OF HARVARD UNIVERSITY]

THE CONSTRICTED MERCURY ARC AS A SOURCE OF LIGHT FOR PHOTOCHEMICAL WORK

BY GEORGE S. FORBES AND GEORGE R. HARRISON[1]

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Any adequate study of reactions having very low photochemical yields, of the reciprocity law and of kindred problems requires very great light intensities produced simultaneously with a high degree of spectral resolution. Dissatisfied with the compromises between these objectives found unavoidable with the usual types of mercury-vapor lamp, we have previously designed and investigated two special lamps.[2,3] The relative intensities of fifteen sets of lines were measured up to extreme conditions of pressure, voltage gradient, current density and constriction of the luminous column.

These researches showed that a constricted arc between two mercury surfaces, confined in a water-cooled quartz tube of 2-mm. internal and 7-mm. external diameter, 38 mm. long with its ends open to the atmosphere, could most nearly meet our requirements.

Our monochromator has been described elsewhere[2] in detail. Fig. 1 gives wave-length energy curves for a constricted arc running on 3 amperes and 90 volts, taken with the monochromator used as a spectro-radiometer, and shows the degree of resolution obtained when the entrance slit was 0.1 mm. wide, and when it was ten times that width. It should be noted that in taking the upper curve, 140 ohms' resistance was introduced in series with the galvanometer and thermopile, so that 1.0cm. deflection corresponded to 1.50 microwatts per sq. mm. at the exit slit, whereas in the lower curve 0.36 microwatt was the corresponding figure. It appears that with the 1mm. entrance and exit slits as commonly used in our instrument, as much (approximately) monochromatic radiation of $\lambda 366$ was transmitted as was received of *total radiation* from the same arc through

[1] National Research Fellow in Physics.

[2] Harrison and Forbes, *J. Optical Soc. Am.*, **10,** 1 (1925).

[3] Forbes and Harrison, *ibid.*, **11,** 99 (1925).

a single slit similar to the exit slit, placed only 14 cm. from the arc with no optical train intervening. The resolution of the instrument was limited in the case of the narrower slit by the aberration of the lenses, due to their large apertures, and where higher resolving power was desired it was necessary to use stops. For work between 200$\mu\mu$ and 300$\mu\mu$,[4] the large quartz prism could be replaced by a water prism having two quartz faces. Along the wave-length axis of Fig. 1 are marked short vertical lines which indicate the number and approximate relative intensities (in a given group) of the various lines making up each maximum, as determined from a spectrogram of the light from the arc taken with an instrument of higher resolving power; the weaker lines, however, are all relatively fainter than indicated in the chart. From this chart an idea can be obtained of the

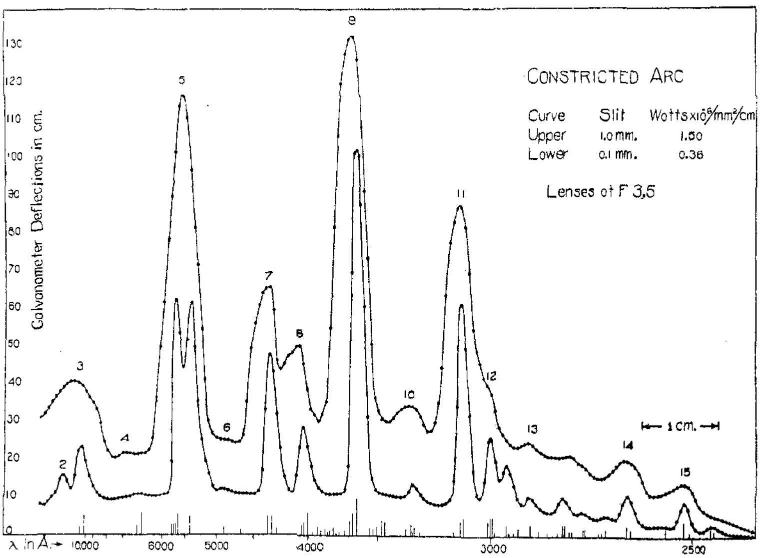

Fig. 1.

wave-length range which would be included in an element of the spectrum transmitted through a slit of given width in a given region. The reference mark 1 cm. wide gives the reduction factor to be used. We compared the constricted arc with a new vertical commercial arc of standard type having sealed-in electrodes and a luminous column 82 × 8 mm. Light intensity, steadiness, life, convenience, economy and efficiency were all considered. It should be borne in mind that the data given will serve only as a general indication of what can be expected from similar arcs and dispersing systems.

Table I shows the relative over-all efficiencies of the two mercury arcs, a gas-filled Mazda lamp being included for reference. For the quartz

[4] Duclaux and Jeantet, *J. phys. radium*, **5**, 92 (1924).

TABLE I

INTENSITY COMPARISONS, 1MM. ENTRANCE AND EXIT SLITS

Maximum Å.		Microwatts per sq. mm. at exit slit Commercial arc	Constricted arc	Constricted arc
5	(5819–5461)	29.4	60.4	326
7	(4359–4348)	12.7	28.8	204
8	(4078–4047)	9.2	17.3	147
9	(3663–3650)	20.0	62.8	490
11	(3132–3126)	11.8	35.4	315
13	(2804)	1.02	2.38	25.0
14	(2700)	2.60	5.88	41.8
15	(2537)	3.76	8.04	36.8
Current, amps.		2.2	1.8	5.0
Voltage, volts		92.0	90.0	97.0
Power, watts		202	162	485
Length, mm.		90.0	38.0	38.0
Watts per cc.		45.0	1350	4050

lamps the spectral range was from about 0.18μ to 7μ, while that of the Mazda lamp was, of course, limited by its glass envelope. It will be seen that under all conditions listed the constricted arc, with its thick walls, even when water-cooled had a total radiation efficiency slightly greater than the normal arc running in an open room at low current and high voltage, but less than the latter when enclosed and permitted to rise in pressure. Where efficiency in the visible and ultra-violet regions only is considered, however, the constricted arc is far superior to the other. The radiation per square centimeter of arc surface is also shown in the table, where the greater intensity of the smaller arc is at once evident. The greater the cooling, the lower the efficiency of the arc in all cases, but thick walls greatly decrease this effect and make possible water cooling, without which the constricted arc could not be operated above 2 amp.

When the need for high intensities is paramount, the voltage gradient (and pressure) should be increased as much as possible, and finally the current raised, keeping cooling at a minimum. But high pressures are troublesome to control, require cumbersome apparatus and produce unsteadiness. The reverse is true when the ends of the lamp are open to constant atmospheric pressure, as a steady state is reached within a minute, as against half an hour required by the sealed-in type; fluctuations of electrical conditions due to variable pressure, so hard to avoid with sealed-in arcs, are prevented. Operating thus with a voltage gradient of 25 v. per cm., a current of 5 amp. furnishes to a slit light intensities many times greater than from a new commercial arc. Such a current, it is true, overloads the constricted arc, and the constriction presently becomes discolored and devitrified. The design of the lamp, however, minimizes these disadvantages, for the operator can empty the lamp; clean it with hydrofluoric acid, dry, revitrify, refill, and boil it out within an hour, all without a pump or special equipment. The equivalent of a new lamp is thus provided. The first cost, needless to say, is very much less than that of a lamp with sealed-in electrodes.

TABLE II

TOTAL RADIATION EFFICIENCY COMPARISONS

Source	Current Amperes	Power Watts	Cooling	Total radiation at 1 meter Watts per sq. mm. × 10^6	Radiation per sq. cm. of luminous column at 1 m. Watts per sq. mm. × 10^6	Relative total efficiency
100-Watt Mazda lamp...	0.90	99	None	3.46	..	0.0350
Commercial arc........	5.0	140	None	1.76	0.24	.0126
Commercial arc........	3.0	270	Enclosed	7.68	1.07	.0284
Constricted arc........	2.0	210	Water	3.10	4.07	.0145
Constricted arc........	3.0	285	Water	3.96	5.2	.0139
Constricted arc........	4.0	388	Water	5.08	6.7	.0131

The actual energy flux obtainable from each lamp behind the exit slit of the monochromator for eight of the more important maxima is exhibited in Table II. Intensities about thrice as great as those listed could have been produced from the commercial arc by materially shortening its life, but its great initial cost and cost of renewal make impracticable energy inputs greater than the normal rating. It will be noted that at the highest intensities used with the constricted arc, 490 microwatts per sq. mm. of approximately monochromatic light of λ366 were issuing from an exit slit 1 × 40 mm., or a total energy flux of about 196,000 ergs per second.

Reeve[5] has collected data on the decline, with time, of the radiation of commercial lamps running at normal power inputs. Apparently, 500 hours of use in a fresh lamp lowers by 60% the radiation λ254, and 28% of λ366, on an average. The constricted arc as used by us is free from the disadvantage of having its walls rendered opaque by spattered tungsten, but the greater concentration of energy used in it shortens its life through devitrification. As the zone of decreased transmission starts at the cathode and works down toward the anode, the constriction could advantageously be lengthened in those cases where 220 v. or more is available. The section next to the anode would then remain unchanged for a greater length of time.

Fig. 2 shows[6] for the constricted arc the rate of decline in energy per sq. mm. of exit slit for λ435, λ366 and λ254. Inverted triangles indicate λ406, upright triangles λ366 and circles λ254. All intensities for λ254 were multiplied by ten before being plotted. The three blacked-in

[5] Reeve, *J. Phys. Chem.*, **29**, 39 (1925).

[6] As data on the life of the lamp were requested by the referee for this paper, Dr. Donald S. Villars, National Research Fellow, kindly communicated the following results, obtained by him while pursuing an independent photochemical investigation in the Chemical Laboratory of Harvard University.

points indicate the sealed-in commercial arc on 82 v. and 4.1 amp. Dotted lines give the output of the constricted arc on 94 v. and 4.9 amp., solid lines the same on 78 v. and 2.1 amp. A new constriction was inserted before the run with 2.1 amp. and this was cleaned and revitrified before that with 4.9 amp. Small corrections have been applied to the ordinates to cancel the effect of small variations in electrical conditions. The commercial arc had been burned but four hours since delivery. One set of readings only was taken from this, running on a wattage somewhat higher than when the data of Table II were obtained. Measurements at λ406, λ313 and λ270 were also made, but are here omitted, as they would complicate the figure without suggesting any further conclusions.

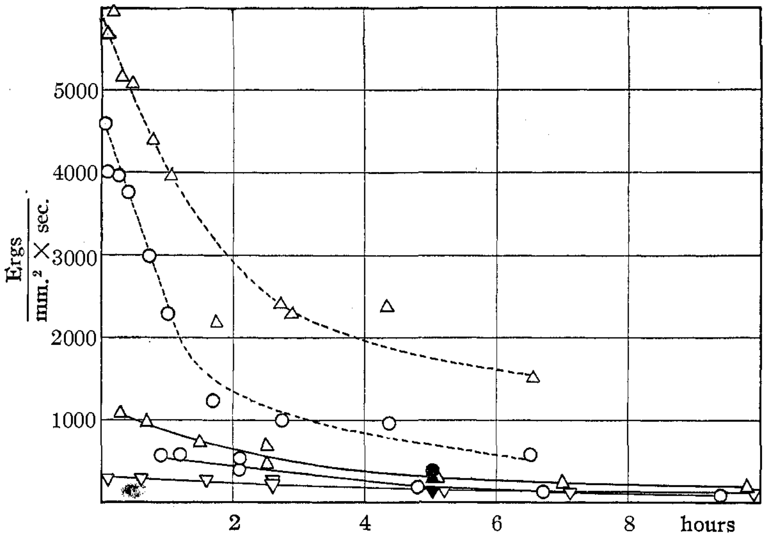

Fig. 2.—Rate of deterioration of lamp.

We are indebted to the Rumford Fund of the American Academy of Arts and Sciences for a grant covering the cost of the constricted arc and of the commercial arc.

Summary

The intensity, steadiness, economy, convenience, efficiency and life of the water-cooled, constricted-column, mercury-vapor lamp run at atmospheric pressure are discussed in comparison and contrast with the standard vertical-sealed-electrode commercial lamp. The constricted arc will furnish, per sq. mm. of exit slit of a monochromator, energy flux up to 30 times that available from a commercial lamp run at normal rating. For quantitative work the radiations of the constricted arc must be followed by a thermopile and the energy integrated graphically. The deterioration of the constricted arc is more rapid, being 50% for the first hour at λ254

and 5 amperes. This rate falls off greatly with increase in time and wave-length and with decrease in current. This is true of all mercury lamps, so that the shorter the wave length used, the more advantageous is the ease of renewal of the open type.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE SEPARATION OF SELENIUM AND TELLURIUM

BY VICTOR LENHER AND C. H. KAO

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Jannasch and Müller[1] in 1898 have claimed that selenium and tellurium can be completely separated in the presence of concd. hydrochloric acid by boiling with hydroxylamine hydrochloride. Their procedure is to dissolve a mixture of the oxides in concd. hydrochloric acid in an Erlenmeyer flask, add 8–10 g. of hydroxylamine hydrochloride and boil for an hour under a reflux condenser. The method has not come into general use, although recently Moser and Miksch[2] studied the method and reported that it is accurate but the precipitation is too slow and too much hydroxylamine hydrochloride is required.

In previous papers[3] the authors have shown that, when sulfur dioxide is added to the hydrochloric acid solution of selenium dioxide, the first stage of the reaction consists in the reduction of tetravalent selenium to selenium monochloride which is volatile when the solution is warmed. Indeed, in the presence of sulfuric acid this reduction makes an admirable method for the preparation of pure monochloride.[3]

That other reducing agents reduce selenium dioxide in hydrochloric acid to the monochloride can be very easily demonstrated. A solution of selenium dioxide in concd. hydrochloric acid, when treated with a warm reducing agent, will assume at first a yellow, then a deep red color, and in a few minutes the monochloride distils. The reducing agents which, when added to selenium dioxide in concd. hydrochloric acid, produce the monochloride are hydrazine hydrochloride, hydroxylamine hydrochloride, sulfur dioxide, metallic tin, aluminum, chromium, manganese, magnesium, iron, cadmium, zinc, lead, arsenic, antimony, cobalt, nickel, bismuth, copper, elementary tellurium, red phosphorus, yellow phosphorus, hydrogen sulfide, cadmium sulfide, zinc sulfide, stannous chloride, ferrous chloride and cuprous chloride. When these reducing agents are added to an excess of selenium dioxide dissolved in hydrochloric acid, the monochloride of selenium is formed. In some cases, as with the active reducing agents, the monochloride forms quickly; in others, it forms slowly. When the

[1] Jannasch and Müller, *Ber.*, **31**, 2389 (1898).

[2] Moser and Miksch, *Monatsh.*, **44**, 349 (1923).

[3] Lenher and Kao, THIS JOURNAL, **47**, 769, 772 (1925).