[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Influence of Several Variables Encountered in Photochemical Work upon the Intensity of Light of λ 254 mμ Produced by a Quartz Mercury Vapor Lamp of the Low Pressure Type Operating in Water at 0 to 95°[1]

BY LAWRENCE J. HEIDT AND HENRY B. BOYLES

A quartz mercury vapor lamp of the low pressure type produces a great deal of light of λ 254 mμ and some of λ 185 mμ, but most of the latter is absorbed in passing through a few cm. of water. We have measured the intensity of the light of λ 254 mμ as a function of the temperature of the water in which the lamp is operated, of the current through the lamp, and of the age of the lamp. Between 0 and 95°, the intensity, I, passes through a sharp maximum at 45°. At 25° the ratio I/i, where i is the current through the lamp, is nearly independent of i for small values of i, but increases rapidly with i at large values of i when the lamp is new. As the lamp ages the ratio I/i decreases for all values of i, but the decrease is especially rapid for large values of i. An evaluation has been made of the extent to which the temperature and current density need to be controlled in order to control the light intensity within prescribed limits.

Photochemical reactions are often carried out most conveniently by employing monochromatic light of λ 254 mμ which can be obtained very pure and up to very high intensities by passing an electrical discharge through mercury vapor at very low pressures. An apparatus designed especially for photochemical work with this light has been described recently.[2] The intensity of the light produced by the apparatus has been found to depend upon the temperature of the lamp, the current through the lamp, the length of time the lamp has been operated, and a few other variables whose influence we have evaluated. The intensity of the light of λ 185 mμ produced by the lamp was not measured since it has been found[3] that none of this light, even when the lamp is new, reaches the reaction vessel after it has passed through a cm. or more of water.

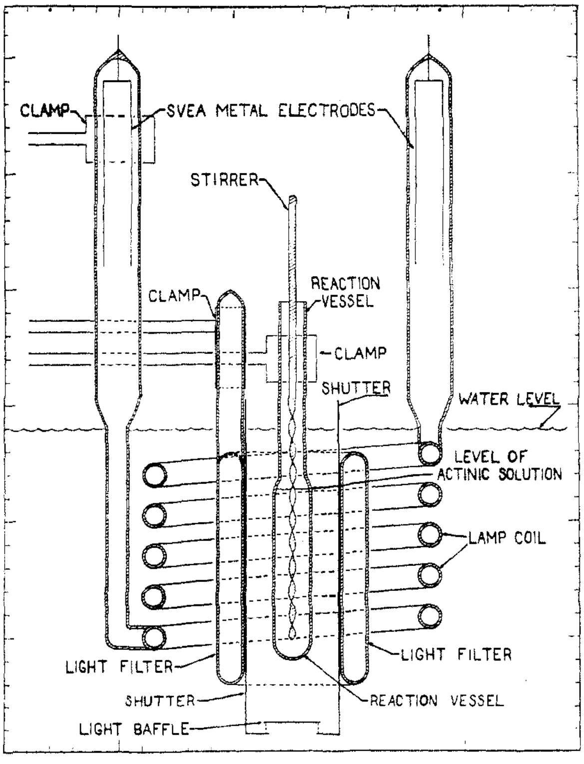

Fig. 1.—Apparatus employed to irradiate solutions with monochromatic light of λ 254 mμ. The sketch is drawn to scale, one small division represents one cm. The parts of the lamp extending above the water level were wrapped snugly with silver foil 0.025 mm. thick. The foil extended about an inch into the water and was coated with silver sulfide. The dense black coating was obtained by immersing the foil in water saturated with hydrogen sulfide at a pressure of 1 atm.

Apparatus and Experimental Procedures.—The lamp, filter, reaction vessel and stirrer were arranged as shown in Fig. 1. The absorbency of the quartz walls of the equipment is given in Fig. 2.

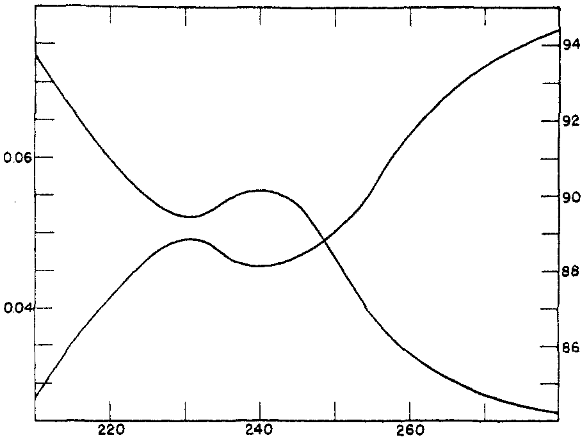

Fig. 2.—Optical density of the fused quartz employed to construct the apparatus. The data are for a flat plate 1.02 ± 0.02 mm. thick and for light perpendicularly incident upon it within ±5°. The curve rising from left to right gives the optical density as read off the left ordinate; the other curve, the per cent. light transmitted. The abscissa gives the wave length of the light in mμ. The quartz walls of the lamp, filter and reaction vessel also were 1.02 ± 0.02 mm. thick.

The lamp was operated by connecting it in series with a luminous tube transformer of the ballast type which was rated to deliver 120 ma. at 7500 v. when connected to a 110 v. a.c. power supply. The current through the lamp was adjusted by changing the voltage drop across the primary coil of the transformer. The radiation produced by the lamp usually reached maximum intensity in less than ten minutes after the lamp had been lit.

The light flux, F, incident upon the solution in the reaction vessel was measured by means of the uranyl oxalate actinometer under the conditions recommended by L. J. Heidt.[3] The actinometer employed to measure high values of F contained 0.017 mole of uranyl oxalate and 0.040

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[1] We gratefully acknowledge the assistance of a grant-in-aid from the Charles F. Kettering Foundation for this work as part of its integrated program on the photosynthesis problem.

[2] L. J. Heidt, *Science*, **90**, 473 (1939).

[3] L. J. Heidt, *J. Phys. Chem.*, **46**, 629 (1942).

mole of oxalic acid per liter of water solution at 25°. The actinometer employed to measure lower values of F contained one-tenth as much of each of these solutes. The uranyl oxalate and oxalic acid were over 99.9% pure except for water of hydration. The actinic solution was stirred continuously while it was being irradiated. The light flux was measured only after the lamp had reached its maximum intensity. The shutter surrounding the reaction vessel then was dropped and the solution was irradiated until the lamp was shut off.

The amount of oxalate destroyed by photolysis was measured by titrating the solution with a solution of ceric sulfate as recommended by G. S. Forbes and L. J. Heidt.[4] End-points were determined by means of a differential electrometric method previously described.[5]

No measurable dark reaction was observed in either of the actinometer solutions under the conditions prevailing during a photolysis even at 95°. This was established by carrying out experiments identical with those employed to photolyze the solutions except that the shutter was not dropped to let the light reach the solution in the reaction vessel.

Evaluation of Light Flux.—The moles of oxalate decomposed by the light, *i.e.*, ΔM, was calculated by means of the equation

$$\Delta M = (12/5)\,(\Delta \text{ ml.})\, C_4/2000$$

where 12 represents the volume in ml. of the actinometer solution that was irradiated in every expt., 5 the volume in ml. of the actinometer solution employed in all titrations, C_4, the concentration of the ceric sulfate in moles per liter, that was used to titrate the actinometer solution, and Δ ml. the difference between the volumes of the ceric sulfate solution required to reach the end-points of the titrations of portions of the actinometer solutions which had and had not been irradiated. The factor 2 allows for the fact that two moles of ceric sulfate are consumed by the oxidation of one mole of oxalate ion or oxalic acid.

The values of the light flux, F, were calculated as quanta per sec. incident upon the 12 ml. of the irradiated solution. This was done by means of the equation

$$F = 6 \times 10^{23}\Delta M/\phi t$$

where ϕ represents the moles of oxalate decomposed per einstein (6×10^{23} quanta) of light absorbed by the actinometer, and t represents the time in seconds the actinometer was irradiated. The value of ϕ for λ, 254 mμ is 0.63 at 25°, but changes with the temperature of the actinometer solution. The increase in ϕ per ten degree rise in the temperature[6] is less than ten per cent. between 15 and 35°, and has not been determined outside of this range. We give, therefore, values of $F^1 = F(\phi/0.63) = 6 \times 10^{23}\,\Delta M/0.63t$ which are larger above and lower below 25° than the values of F.

The dilute and concentrated actinometer solutions both gave the same values of F^1 under the same experimental conditions at all values of the temperature between 0 and 95° and both solutions were found to absorb over 97% of the light of λ 254 mμ incident upon them in the reaction vessel. Thus, ϕ is the same for both the dilute and concentrated actinometer solutions at all temperatures between 0 and 95°.

The light intensity, I, the light flux, F, and the term F^1 are directly proportional to each other, *i.e.*, $I = bF = eF^1$ where b and e are constants when the temperature is held constant. The value of b, but not of e, is independent of the temperature.

Results and Discussion.—Our results are given in terms of the light flux, F, incident upon the actinic solution in the reaction vessel or the modified light flux, F^1, the current, i, through the lamp, the temperature of the water surrounding the lamp, filter and reaction vessel, and the age of the lamp. The age refers to the cumulative time the lamp had been operated, not to its chronological age. All of the data were obtained by employing the same transformer and arrangement of apparatus.

The voltage drop across the lamp depended upon the current, i, the water temperature, and the age of the lamp, decreasing slightly when any of these three variables increased. The values ranged from 700 to 1300 volts.

The electrical energy put into the lamp at a given age was very nearly directly proportional to i since the change in v was small compared to the change in i and for the same reason the light intensity was found to be much more sensitive to changes in the current through the lamp than to the voltage drop across it when the heavily ballasted transformer was employed.

The increase in the light intensity produced by increasing the current through the lamp at 25° is shown in Fig. 3 at several selected ages of the lamp. In the case of small values of i, the light flux and consequently the light intensity is seen to increase linearly with i; *i.e.*, $I = ki$. Aging decreases the value of the proportionality constant k.

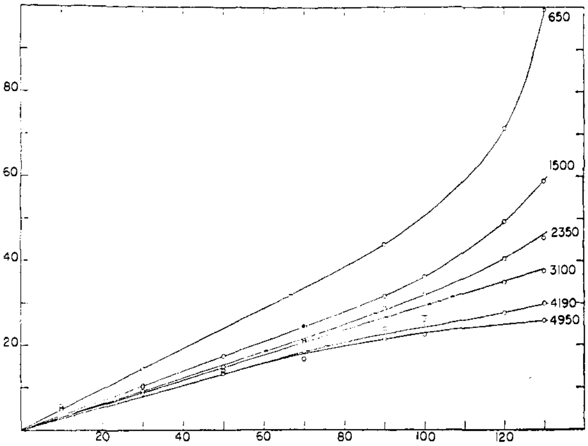

Fig. 3.—Influence of current through the lamp upon the intensity of light of λ 254 mμ at 25°. The age of the lamp is given in minutes alongside the line. The abscissa gives the current in milliamperes, the ordinate gives the light flux in units of 10^{16} quanta per sec. incident upon the 12 ml. of solution in the reaction vessel.

When the lamp is new, the increase in I with i is greater at large than at small values of i as shown by the top line of Fig. 3 where the increase in I between 120 and 130 ma. is 590% greater than the increase in I per 10 ma. over the linear portion of the line between 0 and 70 ma. The advantage of operating at large values of i, however, is gradually lost as the lamp ages because the value of I from an old lamp increases less with i at large than at small values as shown by the two lowest lines in Fig. 3 where the increase in I per 10 ma. between 120 and 130 ma. is only 56% of the increase over the linear portion of the line between 0 and 30 ma. The change of F at a given value of i over the interval of time required to obtain the data represented by any one of these lines was less than ten per cent. as found by occasional redeterminations of F at 70, 90 and 100 ma. during several of these periods.

The decrease in the light intensity as the lamp ages with use is shown in Fig. 4 for several selected values of the current i through the lamp. It will be seen that this decrease is most rapid when the lamp is new and i is large. The deterioration of the

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[4] G. S. Forbes and L. J. Heidt, THIS JOURNAL, **56**, 2363 (1934).

[5] L. J. Heidt, *ibid.*, **61**, 3455 (1939).

[6] G. S. Forbes and W. G. Leighton, *ibid.*, **52**, 3139 (1930).

lamp during the first six hundred minutes was not recorded because of exploratory work.

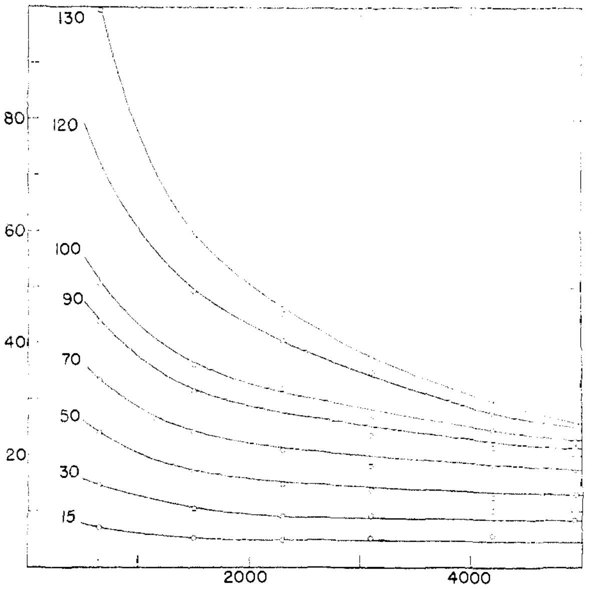

Fig. 4.—Influence of age upon the light intensity at 25°. The curves give the values of the light flux obtained at the recorded values of the current through the lamp. The abscissa gives the length of time in minutes the lamp had been operated, the ordinate gives the light flux in units of 10^{16} quanta per sec.

A thin film of dirt was found to accumulate on the outside of the lamp coil and filter unless these were cleaned often. The dirt collecting on our lamp and filter over a period of about three months decreased the light intensity 40% at all values of i, and our results have been corrected for this effect on the basis that it increased linearly with time. The effect of the dirt was determined by measuring the light intensity immediately before and after scrupulously cleaning the lamp and filter (the reaction vessel was always kept very clean). An additional increase in F of 30% was observed when running tap water was replaced by distilled water. Even when distilled water was employed the lamp and filter needed to be cleaned frequently.

The influence of the temperature upon the light intensity is given in Fig. 5 where F^1 is plotted instead of F for the reasons already stated. The values of F^1 are higher above and lower below 25° than the values of the true light flux, F; so the F^1 curves rise more steeply to their maximum values and thereafter fall more rapidly than I as the temperature is increased. The curves reach their maxima at a temperature about 5° higher than the temperature of maximum light intensity when allowance is made for the increase in ϕ with temperature. The maximum in I consequently occurs at about 45° and is seen from the two sets of curves to be independent of the length of time the lamp has been operated. This temperature is slightly higher than the value of 130°F. (40°C.) reported for the commercial "Sc 2537" lamp.[7]

The character of the light reaching the reaction

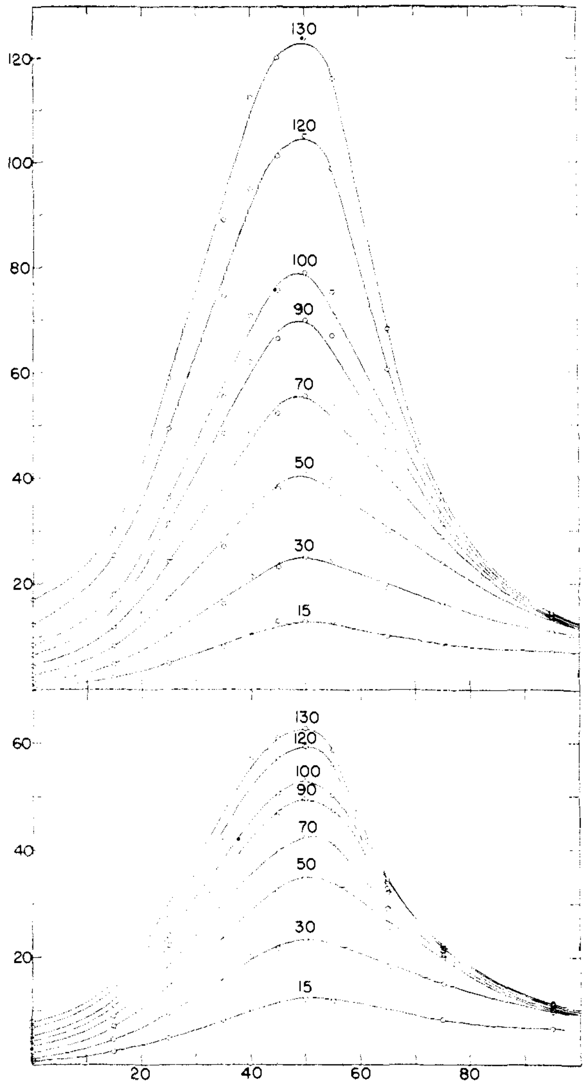

Fig. 5.—Influence of temperature upon the light intensity. The curves give the values of the light flux obtained at the recorded values of the current through the lamp. The abscissa gives the temperature in °C. of the bath of water surrounding the lamp coil, filter and reaction vessel. The upper set of curves represents the results obtained after the lamp had been operated 1500 min.; the lower set represents the results after 4200 min. The ordinates give the values of F^1 in units of about 10^{16} quanta per sec.

vessel is revealed by the following observations. The chlorine filter was found to transmit 75 ± 10% of the actinic light that fell upon it and would otherwise have fallen upon the solution in the reaction vessel at all temperatures between 0 and 95° and at all currents between 15 and 130 ma. This is possible in our experiments only if the light is mainly of λ 254 mμ and the intensities of the wave lengths of other light in the region of the spectrum between 400 and 200 mμ remain small compared to the light of λ 254 mμ in spite of the large increase of over one thousand fold in the pressure of mercury vapor in the lamp from (1.85 to over 1800) 10^{-4} mm. when the temperature is increased from 0 to 95°.

Quantum yields often need to be measured within three per cent. and this can be done only when the

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[7] The "Sc 2537 Lamp" by Hanovia Chemical and Mfg. Co., Newark 5, New Jersey.

light flux is known within 1%. The light intensity ran be controlled within 1% by controlling the current through the lamp within ±1 ma. or ±0.8% between 120 and 130 ma. and within ±0.1 ma. or ±0.6% between 15 and 30 ma., and by controlling the temperature of the lamp within ±0.1° and ±0.05° at 130 and 15 ma., respectively, under the conditions applying to the steep parts of the upper set of curves in Fig. 5. The same degree of control over the temperature, but less control over the current, is required as the lamp ages with use.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KENTUCKY]

The Dielectric Constant of N-Methylamides

BY GORDON R. LEADER[*] AND JAMES F. GORMLEY

Dielectric constants have been determined in the temperature interval 15–35° for monomethyl-formamide, acetamide and propionamide, for dimethylformamide and acetamide and for ethyl N-methylcarbamate. The values observed are interpreted in terms of the influence of steric properties of the molecules upon association through hydrogen bonding.

Liquids associated through hydrogen bond formation have been shown by Kumler[1] to deviate markedly from a semi-empirical relationship which applies satisfactorily to many liquids in which the association is due largely or entirely to dipole interaction. The dielectric constants of hydrogen-bonded liquids are found to be either much higher than expected in cases where the hydrogen bonding produces extended "polymers" having increased dipole moments, or much lower in those cases where the association, as in acetic acid, leads to formation of a dimer of small or zero moment.

Measurements of the dielectric constants of monomethylamides which are here reported have shown them to be unusually high. These compounds are especially inclined to associate as extended polymers because of the presence in each molecule of only two sites able to participate in hydrogen bond formation, and because of a *trans* disposition of these sites, as shown by Mizushima[2] from Raman spectra and infrared studies on N-methylacetamide. For the structurally similar compound ethyl N-methylcarbamate a relatively low dielectric constant has been observed, indicating that the compound is largely dimerized because of a *cis* structure of the monomer. The data thus serve to illustrate the important role played by steric factors in determining the effect of hydrogen bonding on the orientation polarization of this class of compounds.

Experimental

Apparatus.—Dielectric constants were measured using a modified cell of the type devised by Conner, Clark and Smyth[3] together with a General Radio Twin-T Impedance Bridge as previously described.[4] For measurements with liquids of very high dielectric constant, a special cell having the constants: $C_0 = 1.9\ \mu\mu f.$ and $C_v = 1.765 \pm 0.003$ was constructed. The cells used were calibrated using purified benzene[5] methanol and water[6] as standard liquids. Measurements were made at a frequency of 10 mc. in most cases and were corrected for errors due to inductance in both the bridge circuit and cell by determining differences between measured capacities of the cell at 1 mc. and 10 mc. when filled with methanol, water and methanol–water mixtures. These sufficed to establish a partial correction curve for the inductance errors at low measured capacities and permitted estimation of the cell inductance by use of which the corrections at higher capacities could be calculated.[7]

Temperatures were measured with a 0.1° thermometer calibrated by the National Bureau of Standards. Refractive index measurements were made with a Spencer Abbe Refractometer. Density measurements were made using a Regnault pycnometer of 50-cc. capacity.

Materials.—N-Methylformamide was prepared by reaction of 98–99% formic acid with gaseous methylamine until the required weight was absorbed. The resulting concentrated salt solution was then heated at 160–170° at atmospheric pressure to drive off water and form the amide. When the water had been removed, the pressure was gradually reduced and the product was finally purified by fractionation under vacuum through a 35 × 1 cm. glass helices packed column. The distilled material was further purified by successive crystallizations. This procedure gave material of high purity as indicated by its melting point, but its conductivity was too high to permit dielectric constant measurements. To reduce the conductivity, about 200 cc. of purified liquid was slowly passed through a 10 × 1 cm. column packed with dried Amberlite IR-120 in the hydrogen form. This treatment effectively reduced the conductivity by converting methyl ammoniumformate to formic acid which, as has been observed for acetic acid in formamide,[8] is only slightly dissociated in the N-methylformamide medium. The first portions of N-methylformamide to come through the column were contaminated with water displaced from the resin, but later portions finally reached a limiting high value of dielectric constant, indicating that no more water was present. Conductivity of the material used for measurements was about 5×10^{-5} ohm^{-1} cm.$^{-1}$, d^{25}_4 0.9976, n^{25}_D 1.4310, m.p. −3.8°; lit.[9] 0.9961, 1.4300, −5.4°.

N-Methylacetamide.—A commercial product was purified by crystallization; sp. cond. about 10^{-6}; d^{30}_4 0.9512, n^{30}_D 1.4290, m.p. 29.7°; lit.[9] 0.9517 (25°), 1.4301 (25°), m.p. 28.0°.

N-Methylpropionamide was prepared from propionic acid and methylamine as described for N-methylformamide. The product was purified by fractionation under vacuum; b.p. 134° at 60 mm.; sp. cond. about 10^{-6}; d^{25}_4 0.9306, n^{25}_D 1.4350; lit.[9] 0.9304, 1.4345.

N,N-Dimethylformamide and N,N-Dimethylacetamide.—Commercial material was purified by fractionation at atmospheric pressure after treatment with solid KOH and CaO; d^{25}_4 0.9442, n^{25}_D 1.4290(DMF); d^{25}_4 0.9365, n^{25}_D 1.4363-(DMA); lit.[10] 0.9445, 1.4269; 0.9366, 1.4351.

Ethyl N-Methylcarbamate.—Commercial material was purified by distillation; b.p. 169–170 at 740 mm.; d^{25}_4 1.0042, n^{25}_D 1.4179; lit.[11] 1.0087 (19°), 1.4200 (19°).

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[*] Mallinckrodt Chemical Works, St. Louis, Mo.

[1] W. D. Kumler, THIS JOURNAL, **57**, 600 (1935).

[2] S. Mizushima, *et al.*, *ibid.*, **72**, 3490 (1950).

[3] W. P. Conner, R. P. Clark and C. P. Smyth, *ibid.*, **64**, 1379 (1942).

[4] G. R. Leader, *ibid.*, **73**, 856 (1951).

[5] R. M. Davies, *Phil. Mag.*, **21**, 1 (1936).

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[7] I. G. Easton, "Corrections for Residual Impedances in the Twin-T," General Radio Co., Cambridge, Mass.

[8] W. J. McCreary, M.S. Thesis, Univ. of Kentucky, 1948.

[9] G. F. D'Alelio and E. E. Reid, THIS JOURNAL, **59**, 109 (1937).

[10] J. R. Ruhoff and E. E. Reid, *ibid.*, **59**, 402 (1937).

[11] O. Schmidt, *Ber.*, **36**, 2476 (1903).