LXXII.—*The Distribution of Energy in the Radiation from the Uviol-glass Lamp.*

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A NUMBER of photochemical investigations have been carried out in the past, and will doubtless be carried out in the future, in which the Schott mercury Uviol-glass lamp is used as the source of radiation, monochromatic illumination, if aimed at, being obtained by the use of filters. In order to utilise fully the results of these investigations, a knowledge of the distribution of energy in the different parts of the spectrum of the lamp is necessary.

In default of direct determinations of this distribution, it has been assumed by some workers (Luther and Forbes, *J. Amer. Chem. Soc.*, 1909, **31**, 780; Plotnikov, *Zeitsch. physikal. Chem.*, 1912, **79**, 642) that the values obtained by Ladenburg (*Physikal. Zeitsch.*, 1904, **5**, 525; measurements of less value for this particular purpose were made by Pflüger, *Ann. Physik*, 1908, [iv], **26**, 789) for the quartz mercury lamp could be employed. Owing, however, to the greater transparency of quartz as compared with uviol-glass even for the less refrangible regions of the ultra-violet, it is unlikely, as was pointed out by Winther (*Zeitsch. Elektrochem.*, 1913, **19**, 395) and by Bruner (*ibid.*, 555) that calculations made on this basis are of any value.

The first attempt to measure directly the ratios in question for

the Uviol lamp we owe to Winther (*loc. cit.*), who employed the "fluorometer" designed by him. The following table contains in the first column the values for the intensities of certain bands of the quartz mercury lamp, referred to the blue band as unity. These values are taken from the graphical integration of Ladenburg's measurements carried out by Plotnikov ("Photochemische Versuchstechnik," 1912, 17—19). The second and third columns contain Winther's values for the quartz and uviol-glass lamps:

Band.	Quartz (L.)	Quartz (W.)	Uviol (W.)
436 $\mu\mu$	1.00	1.00	1.00
405	0.54	0.62	0.29
362	1.83	2.31	0.25
313	1.28	0.87	0.045
302	—	0.29	—
254	0.20	0.23	—

The agreement between Ladenburg's and Winther's ratios for the quartz lamp is, on the whole, exceedingly good. The biggest percentage deviation is shown in the case of the 362 $\mu\mu$ (ultraviolet) band. Plotnikov's integration of Ladenburg's figures for the 313 $\mu\mu$ band also includes the 302 $\mu\mu$ band, and one should strictly compare about two-thirds of his value of 1.28 (that is, 0.86) with Winther's figure of 0.87, or else the sum of Winther's values for the 313 $\mu\mu$ and 302 $\mu\mu$ bands (that is, 1.16) with his figure of 1.28. Winther's figures for the Uviol lamp indicate, as would be expected, that the intensities of the ultra-violet bands, compared with the blue band, are far less than for the quartz lamp, and also, which is more surprising, that the relative intensity of the violet band (405 $\mu\mu$) is also considerably less.

This is not the place to criticise the principle involved in Winther's method. Various figures given in the course of his interesting paper, as well as the ratios for the quartz lamp quoted above, show that it is capable of giving results of a very fair degree of accuracy in many cases. It may, however, be pointed out that the intensity of fluorescent light produced by his comparison standard source is strictly given by:

$$I' = \int_{\lambda_1}^{\lambda_2} k_{\lambda} I_{\lambda} 10^{-m_{\lambda}(5-d)}.$$

(where I' is the total intensity of fluorescent light, k_{λ} , I_{λ} , m_{λ} are respectively the fluorescence factor, intensity of the source, and extinction-coefficient for the wave-length λ ; and λ_1 and λ_2 represent the limits of the spectrum capable of exerting fluorescence), and not by:

$$I' = kI10^{-m_{\lambda}(5-d)}.$$

(where I is the [constant] total intensity of the comparison source,

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and k and m_n are mean values for the fluorescence factor and the extinction-coefficient). The fact that one variable (m_n) occurs in the exponent, whereas the others do not, renders it in theory impossible to get a really satisfactory value of m_n , a magnitude essentially involved in all measurements made with the instrument. Winther quotes mean values of m_n , determined for various fluorescing solutions by measurements of the standard comparison source against monochromatic light of different wave-lengths, and it would be interesting to know how far the separate values thus obtained differ amongst themselves. Apart from this objection, the actual error in reading may amount to as much as 20 per cent. with weak sources of light (although this can be considerably reduced by repeated observations), and slight variations in the standard lamp may also prove of importance. Plotnikov (*Zeitsch. Elektrochem.*, 1913, **19**, 754) estimates the accuracy of the apparatus as 20—30 per cent. As it is particularly when measuring comparatively weak sources of radiation, the quality of which considerably differs from that of the comparison source, that we should expect these different factors to count, it seemed desirable to investigate the distribution of the energy in the Uviol lamp by an independent method.

The method chosen was that used by Ladenburg (*loc. cit.*) for the quartz lamp, namely, direct measurement of the intensity of the different bands by means of a thermopile. The Uviol lamp was burnt under constant conditions of current and voltage at some distance from a Hilger monochromatic illuminator, on the front slit of which an image of the lamp was thrown by means of a quartz lens. A large, water-cooled screen protected the instrument from direct radiation from the lamp, and the slit could be illuminated by means of a water-cooled shutter. The dispersed light passed through the second slit of the instrument on to a Hilger thermopile placed immediately behind it, the thermopile being short-circuited on to a Paschen galvanometer, the coils of which had the same resistance as that of the thermopile, namely, about three ohms. Unfortunately, the Paschen galvanometer, although exceedingly sensitive, and, owing to the lightness of its suspension, scarcely affected by incidental mechanical shaking, is very subject to external magnetic disturbances, and its design renders it difficult to shield effectually. Consequently, although it was almost completely surrounded by 5 cm. of soft iron wire wound on a vertical drum, with 2.5 cm. of transformer plates above and below, it was impossible to work with it in the daytime. All definitive measurements were carried out at night, and even then its sensitiveness had to be reduced to 10^{-1} — 10^{-2} of its maximum value

to obtain a zero steady enough with which to work. Further, the low dispersion of the quartz prism of the monochromatic illuminator made it necessary to work with comparatively narrow front and back slits if the different bands after dispersion were to be completely separated. Thus the amount of energy entering the instrument was low, and the surface of the thermopile was only partly utilised, and these factors, combined with the low sensitivity of the galvanometer, resulted in very small deflexions, varying, according to width of slit, position of band, and sensitivity of galvanometer, between 0.8 and 50 mm., and being mostly less than 1 cm.

In order to measure such deflexions at all satisfactorily with a galvanometer the zero of which was continually changing, the readings had obviously to be repeated a large number of times. As two kinds of change of zero had to be contended with, namely, a gradual drift in one particular direction, and smaller changes occupying a fraction of a second, the method of measurement adopted was as follows: Six readings were taken at rapid and regular intervals with the shutter down. Their mean is denoted by Z_0 . The shutter was then raised, and six more readings were taken in the same way, their mean being denoted by R_1 . A cycle of twelve readings required about one minute. Six more readings of the zero were then taken (shutter down), their mean giving a value Z_1 , and the procedure was repeated until twenty-one sets of six readings had been taken, the last set always being made with the shutter down, and the whole operation occupying about ten minutes. The values of the deflexions obtained under these conditions were given by:

$$R_1 - \left(\frac{Z_1 + Z_0}{2} \right) = D_1,$$

$$R_2 - \left(\frac{Z_2 + Z_1}{2} \right) = D_2,$$

$$R_{10} - \left(\frac{Z_{11} + Z_{10}}{2} \right) = D_{10},$$

and the mean of the different values of D was taken as representing the deflexion for the band in question. The extreme variation between the different values of D was about 50 per cent. with small, 15 per cent. with large deflexions, and the probable error in the final value of D varied between 5 and 20 per cent.

That this method is capable of giving satisfactory results is shown by the following figures obtained in different series of experiments:

Deflexion given by		Ratio of deflexions.
436 $\mu\mu$	313 uu	
7.6 mm.	1.3 mm.	0.17
46.9	8.1	0.17
35.2	5.9	0.17

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Deflexion given by		Ratio of deflexions.
436 $\mu\mu$	362 $\mu\mu$	
8.1 mm.	3.2 mm.	0.40
7.6	3.1	0.41
7.6	2.7	0.35
3.0	1.3	0.43

Most of the definitive measurements were carried out with a front slit of 0.4—0.5 mm. width and back slit 0.4—0.8 mm. For the ultraviolet bands it was possible to use wider slits, but the green and the yellow bands were only just separated with the narrowest slits used. The actual intensity ratios of yellow/blue and green/blue are to be looked on as merely preliminary. On the other hand, there is little doubt that the sum of the intensities of the green and the yellow bands is, as will be seen, substantially equal to the intensity of the blue band. Several experiments gave this result. In all cases, with the exception of the ultraviolet band 313 $\mu\mu$, the width of the band measured was taken from the diagram on p. 18 of Plotnikov's "Photochemische Versuchstechnik." The band specified was measured between the limits 300—320 $\mu\mu$.

The lamp used was run off the 230-volt mains in series with a resistance and an inductance. It usually took about an hour to attain constant values of current and voltage. Measurements were made with:

- (a) 3.5 amperes and 56 volts,
- (b) 3.2 amperes and 34 volts,

and practically identical values for the intensity ratios were obtained.

Column 1 of the following table contains the values finally obtained, referred to the intensity of the blue band as unity. Columns 2 and 3 contain respectively Winther's figures for the Uviol lamp and Ladenburg's figures for the quartz lamp:

	Uviol (A).	Uviol (W).	Quartz (L).
571 $\mu\mu$	0.27	—	2.63
541	0.73	—	3.93
436	1.00	1.00	1.00
405	0.56	0.29	0.54
362	0.42	0.25	1.83
313	0.17	0.045	1.28 (0.86)

Comparing columns 1 and 2, the values for the three most refrangible bands are seen to be considerably greater than Winther's figures. Columns 1 and 3 lead to the conclusion that, whilst the relative intensities of the blue and the violet bands are the same in the quartz and the uviol-glass lamps, and the relative intensities of the ultraviolet bands far less for the Uviol lamp, this last statement also holds good for the green and the yellow bands, which is an unforeseen result.

It remains to apply, if possible, the above figures to already existing photochemical data obtained with the Uviol lamp. This can only be done approximately and with a great deal of uncertainty. Spencer (T., 1914, 105, 2572), who made use of Winther's light-filters and Winther's figures for the distribution of energy, points out that the velocity of decomposition of a sodium hypochlorite solution for a given intensity of light appears to be greater the shorter the wave-length of the active radiation. Assuming that Winther's filters are correct (which is at all events approximately true), and that the three thicknesses of Uviol glass used between the lamp and the hypochlorite solution did not selectively affect the intensities of the different bands (this is less likely to be correct), the ratios of the velocity-coefficients obtained become:

436 $\mu\mu$		1.0	(1.0)
405		2.2	(4.3)
362		4.3	(7.1)
313		4.4	(16.3)

Spencer's values are bracketed. The absolute values of the ratios are considerably altered, but the order remains unchanged.

It has been proposed by Bruner (*loc. cit.*) that the velocity of a photochemical reaction is proportional to the energy absorbed, and independent of the frequency of the light. Certain experiments by Lasareff (*Ann. Physik.*, 1907, [iv], 24, 661) on the bleaching of organic dyes appear to support this view; others (*ibid.*, 1912, [iv], 37, 812) by the same author are not in accord with it. This last statement also holds good of the experiments of Henri and Wurmser (*Compt. rend.*, 1913, 156, 3) on the action of ultraviolet light on acetaldehyde. Bruner attempted to show that experiments of Plotnikov (*Zeitsch. physikal. Chem.*, 1912, 79, 641) on the photochemical addition of bromine to cinnamic acid agree with his view. In the opinion of the present writer too many assumptions and approximations are involved to justify any conclusions drawn from those experiments. The only experimental work that can be utilised with advantage in this connexion is the investigation of the photochemical oxidation of quinine by chromic acid carried out by Luther and Forbes (*loc. cit.*). Assuming complete absorption of the 406 $\mu\mu$ and 362 $\mu\mu$ bands, these workers found the ratios of the velocity-constants to be:

$$\frac{k_{406}}{k_{362}} = \frac{1.00}{0.82}.$$

The figures obtained in the present paper indicate:

$$\frac{i_{406}}{i_{362}} = \frac{1.00}{0.75}.$$

The agreement is good, and the discrepancy certainly not greater than the various experimental errors involved.

The author would finally point out the importance of knowing, and, if necessary, measuring, the extinction-coefficients, not only of the different liquid and gaseous systems on which the action of light is being studied, but also of the materials of the vessels containing such systems. Photochemical measurements carried out without a knowledge of these magnitudes and without tried and suitable filters to secure essentially monochromatic light lose the greater part of their value.

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