CXV.—*The Origin of the Ultra-violet Spectrum of the Glow of Phosphorus.*

By HARRY JULIUS EMELÉUS and RONALD HERBERT PURCELL.

THE spectrum of the light from glowing phosphorus is continuous in the visible region and shows five groups of bands in the ultra-violet at about λ 3419—3245, 2633—2594, 2552—2527, 2477—2451, 2393—2371 Å.U. (Centnerszwer and Petrikaln, *Z. physikal. Chem.*, 1912, **80**, 235; Petrikaln, *Z. Physik*, 1924, **22**, 119). They have been observed in the normal flame of phosphorus (Emeléus and Downey, J., 1924, **125**, 2491), in the glow of phosphorus trioxide, and in the flame of phosphine (Emeléus, J., 1925, **127**, 1362). The band at λ 3270 was recorded by Hartley (*Phil. Trans.*, 1894, **185**, 168); who introduced phosphorus pentoxide into the oxy-hydrogen flame. These bands were also measured by Geuther in a comprehensive survey of the phosphorus spectra (*Z. wiss. Phot.*, 1907, **5**, 33); he obtained them, together with other bands apparently not present in the glow, on volatilising potassium phosphate in the carbon arc. Other ways of producing what is apparently the same spectrum are described in Kayser's Handbuch (Vol. VI), but from none of these methods can the origin of the bands be determined unambiguously.

The experiments described below consist in an examination of the ultra-violet spectrum of the phosphorescence of phosphorus pentoxide, and of the discharge through its vapour. Ebert and Hoffmann (*Z. physikal. Chem.*, 1900, **34**, 80) found that phosphorus pentoxide exhibited a strong phosphorescence after illumination, especially at low temperatures. They recorded the visible spectrum as continuous, with a maximum intensity in the green, a result which was confirmed in the present work during an unsuccessful search for ultra-violet bands. The discharge through phosphorus pentoxide vapour gave a complex band system, in which were included the bands of the spectrum of glowing phosphorus. Finally, a re-examination of the latter phenomenon was made, revealing other bands common to these two spectra.

The Spectrum of the Phosphorescence of Phosphorus Pentoxide.—The spectrographs used were a Hilger quartz instrument (size E6), for the loan of which the authors are indebted to the Air Ministry, and a large-aperture quartz spectrograph of special construction. This had two lenses working at an aperture of f 4·5 and a Cornu prism of 7·5 cm. base. The dispersion at λ 2550 was approximately 30 Å.U. per mm.

The apparatus used in photographing the spectrum of the phosphorescence at liquid-air temperatures is shown in Fig. 1. Pure phosphorus pentoxide was distilled in a vacuum on to the outer surface of the inner tube, T, from a tube having a ground glass

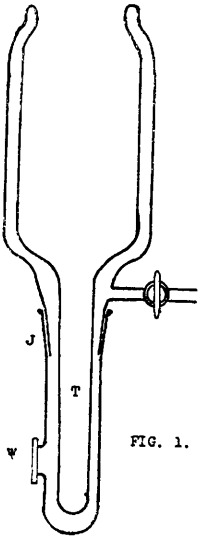


FIG. 1.

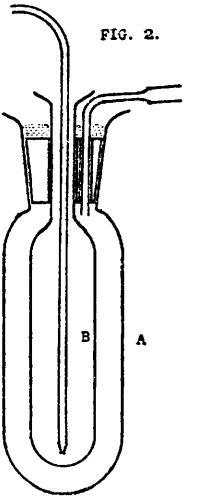


FIG. 2.

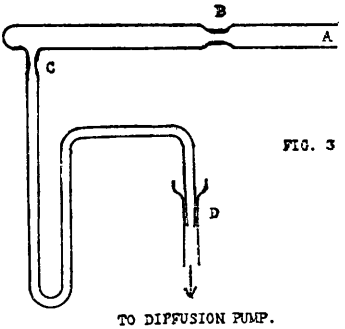


FIG. 3

joint interchangeable with J. The outer tube (shown in position), with a quartz window, W, attached by wax, was then quickly replaced and the interspace was kept exhausted by a diffusion pump. Liquid air was poured into the inner tube, T, as required.

In Fig. 2 is shown a simpler device used for studying the phosphorescence of phosphorus pentoxide cooled to about $-50°$ by carbon dioxide. The outer tube, A, was of clear quartz, and phosphorus pentoxide was sublimed directly from it on to the inner tube. Cooling was effected by carbon dioxide, which was delivered from a cylinder and passed through a fine jet at the end of a copper tube inserted into the inner vessel.

The relatively feeble phosphorescence at the ordinary temperature was photographed by filling a silica tube with the pentoxide.

Blank experiments were made to examine the phosphorescence of the silica tube itself.

The pentoxide was illuminated in each case by a condensed spark between aluminium poles placed 1 cm. from the apparatus containing the oxide. A jet of water playing on the silica opposite the spark kept the surface clean. A sector, synchronised with the spark, rotated between it and the slit of the spectrograph, placed in alinement. The pentoxide was illuminated by the spark during one-quarter of each revolution of the sector, the speed of which was varied according to the duration of the phosphorescence (which was determined by the temperature). The actual exposure of the phosphorescence was about two-thirds of the period of each revolution.

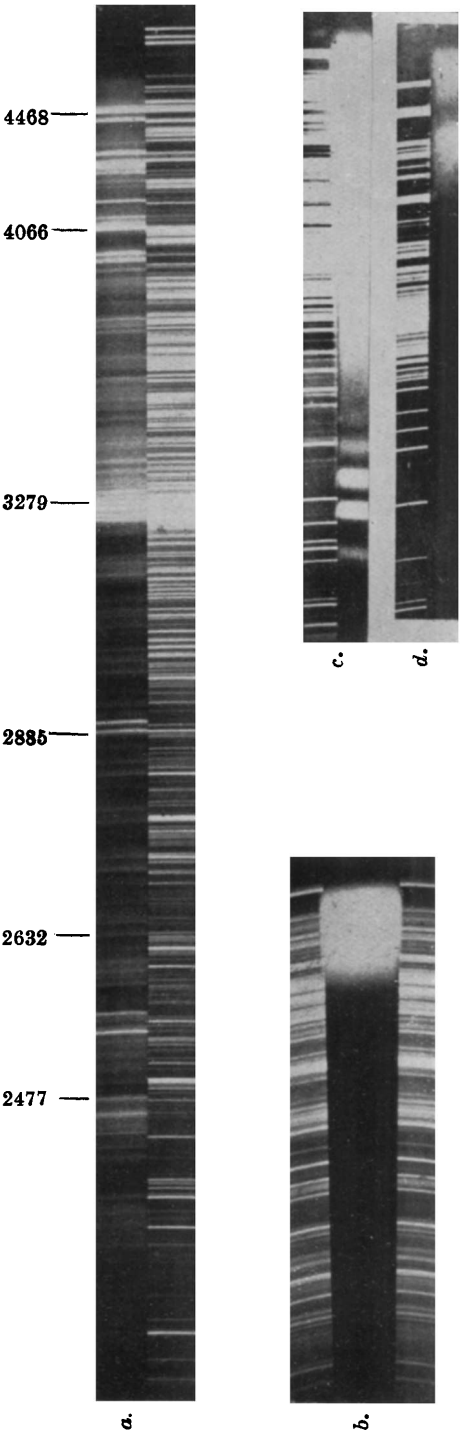
Exposures of 10—140 hours were made under the various conditions specified; in each case the band in the visible region with a maximum intensity at about λ 4600 was observed, using Ilford Monarch plates (compare Ebert and Hoffmann, *loc. cit.*). There was no evidence of an ultra-violet spectrum. A photograph showing this band is given in Plate 1 (*b*). It corresponds roughly with a broad band in the spectrum of the visible light from glowing phosphorus [Plate 1 (*d*)]. This suggests that the latter is due to the phosphorescence of phosphorus pentoxide under the action of the ultra-violet radiation emitted in the reaction.

Spectrum of the Discharge through the Vapour of Phosphorus Pentoxide.—The phosphorus pentoxide was contained in a silica tube (18 cm. long, 0·8 cm. internal diameter) with a clear end, the method of filling being as follows. The silica apparatus ACD was cleaned, dried, and connected to a diffusion pump by a mercury-sealed ground joint, D. A quantity of pure phosphorus pentoxide was introduced into BA, which was then sealed at A in the oxy-hydrogen flame. The apparatus was exhausted, with the U-tube cooled in liquid air, BC was baked out, and AB warmed. The pentoxide was distilled into BC, and AB was sealed off at the constriction B. After distilling the pentoxide four times from one end of BC to the other with the pump working, in which process much of it was transferred to the U-tube, the constriction C was sealed.

External electrodes of copper foil, with a condenser and spark-gap in the circuit, were used in exciting a discharge through the tube, which was heated electrically to 200°. The discharge was dim, and of a greenish-white colour. Exposures of up to 40 hours were needed on the Hilger spectrograph.

A complex band spectrum was observed, which was compared directly with a spectrogram of the glow of phosphorus taken on the

PLATE 1.



(a) *Spectrum of discharge through phosphorus pentoxide vapour (2 hours).*
(b) *Spectrum of phosphorescence of phosphorus pentoxide at −55° (45 hours).*
(c) *Spectrum of glow of phosphorus (480 hours).*
(d) *Spectrum of glow of phosphorus on panchromatic plate (250 hours).*
Copper-arc reference spectra.

[*To face page* 790.]

same instrument. There was no doubt that the bands in the glow spectrum were present in the discharge, although in the latter there were many additional bands, and the isolated groups were connected by bands of low intensity. Most were narrow and degraded towards the red. The positions of the violet edges, which were fairly sharp, were measured. In certain cases, where there was no definite head, the approximate position of the violet edge of the band was again ascertained. Plate 1 (*a*) is an enlargement of this spectrum, showing the groups of narrow bands below λ 3000, and also the complex band at λ 3300—3200. Only the more intense band heads above λ 3000 are recorded, the dispersion of the instrument being small. The two narrow bands at λ 2896 and 2885 are attributed to carbon.

Table of Wave-Lengths of Violet Edges of Bands.

λ.	λ.	λ.	λ.	λ.	λ.	λ.
4468 (7)	3493 (4)	3211 (3)	2896 (7)	2689 (2)	2534 (7)	2425 (4)
4346 (9)	3469 (6)	3135 (6)	2885 (8)	2665 (4)	2533 (4)	2421 (2)
4276 (6)	3313 (4)	3129 (3)	2861 (3)	2646 (4)	2526 (2)	2405 (1)
4119 (7)	3303 (4)	3124 (3)	2840 (4)	2632 (4)	2511 (2)	2392 (2)
4066 (10)	3287 (3)	3064 (3)	2823 (4)	2617 (2)	2499 (4)	2380 (3)
3944 (7)	3279 (4)	3045 (4)	2806 (3)	2602 (4)	2488 (4)	2376 (2)
3911 (7)	3270 (6)	3008 (4)	2778 (4)	2593 (5)	2477 (5)	2368 (1)
3747 (6)	3266 (6)	2937 (3)	2762 (4)	2580 (5)	2464 (4)	2353 (2)
3726 (5)	3256 (6)	2921 (3)	2720 (1)	2553 (5)	2445 (6)	2343 (2)
3517 (4)	3246 (6)	2912 (3)	2705 (5)	2546 (4)	2432 (6)	2318 (2)

The error in the measurements below λ 3000 is probably less than 2 Å.U. The bands between λ 2200—2800 and the complex band at λ 3100—3400 appear to correspond in part with the more precise measurements of Geuther, de Watteville, and de Gramont (Kayser, *op. cit.*, p. 253), but the spectra are not identical. This can be ascribed to the low dispersion of the instrument, and the different means of excitation used in the present research. The description of this spectrum does not come within the scope of this paper. It is intended to attempt to correlate it with the absorption spectra of the oxides of phosphorus.

From these results it was concluded that the band spectrum observed in the discharge through phosphorus pentoxide was emitted from the molecule of an oxide, and that the spectrum of the glow of phosphorus had the same origin.

Re-examination of the Spectrum of the Glow of Phosphorus.—The bands described by Geuther (*loc. cit.*) include groups of low intensity at λ 2789—2647, and a group at λ 2320—2280. These and other bands observed in the discharge through phosphorus pentoxide had not been observed in the spectrum of the glow of phosphorus. The large-aperture quartz spectrograph was therefore used in a re-

examination of this phenomenon. The light source was a phosphorus slab cast in a tray (Centnerszwer and Petrikaln, *loc. cit.*).

With an exposure of 480 hours the five groups of bands already known were observed. Some of the negatives showed the components of each group. The continuous spectrum extended to λ 2700, partly obscuring the band at λ 3270. Three new broad bands were also visible, although the component narrow bands of each of these groups could not be distinguished. Their approximate positions were λ 2300—2325; 2660—2700; 2740—2795. Of these new groups, only one (that at λ 2660—2700) has been satisfactorily reproduced in Plate 1 (*c*). They correspond with groups of bands recorded by Geuther, which are also present in the spectrum of the discharge through phosphorus pentoxide vapour, a fact which supports the view put forward as to the origin of the spectrum of the glow of phosphorus. A further exposure of 250 hours on a panchromatic plate showed that the spectrum of the glow of phosphorus extended into the red. What are apparently two broad bands occur at λ 5200—5900, and λ 6000—6800. The dispersion of the instrument is too small to determine if these are due to the merging of narrower bands.

Summary.

Attempts have been made to determine the origin of the spectrum of the glow of phosphorus by unambiguous means. The ultra-violet spectrum of the phosphorescence of phosphorus pentoxide was first photographed, and exhibited none of the bands occurring in the spectrum of the glow of phosphorus. The discharge through the vapour of phosphorus pentoxide in a silica tube gave a complex band spectrum, which included all the bands known in the spectrum of the glow of phosphorus. A re-examination of the latter phenomenon showed further bands common to these two spectra. It was concluded that the ultra-violet spectrum of the glow of phosphorus had its origin in the molecule of an oxide.

We wish to thank Professor H. B. Baker, F.R.S., in whose laboratory these experiments were carried out, for his keen interest and advice. We are greatly indebted to Professor A. Fowler, F.R.S., who has placed facilities at our disposal and advised us in the interpretation of the spectra. We also wish to thank Dr. W. E. Downey, who developed the apparatus and technique used in studying the phosphorescence of phosphorus pentoxide at liquid-air temperatures, for kindly giving us the benefit of his experience. One of us (R. H. P.) is in receipt of a maintenance grant from the Department of Scientific and Industrial Research; the other holds

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