LXXXV.—*The Origin of the Spectrum of the Glow of Phosphorus.*

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IN a recent paper (J., 1927, 788) the authors described the spectrum produced by passing a discharge through phosphorus pentoxide vapour. It was pointed out that it corresponded in part with the ultra-violet band spectrum of the glow of phosphorus, and the conclusion was drawn that both spectra had their origin in the molecule of an oxide. Dr. R. C. Johnson, to whom we are deeply indebted, has since pointed out to us that the measurements recorded for the discharge through phosphorus pentoxide correspond below 3000 Å. with the bands of the singly ionised oxygen molecule (Johnson, *Proc. Roy. Soc.*, 1924, *A*, **105**, 683); at longer wave-lengths our measurements, which were made on a Hilger small quartz spectrograph, do not furnish a sufficiently accurate basis for comparison. The same spectrum was observed by Stuchtey (*Z. wiss. Phot.*, 1920, **19**, 161) in the thermal decomposition of ozone. From this evidence it might be concluded that the ultra-violet light emission from glowing phosphorus is due to oxygen, a view of considerable interest because of the formation of ozone in the reaction. This idea is based on the identity of the spectra, and since the observations on the phosphorus glow leave much to be desired both in accuracy and in

completeness, owing to the feebleness of the light source, a careful re-examination of the evidence has been made.

A table for comparing the spectroscopic results was constructed from Johnson's measurements and those relating to the glow of phosphorus (Centnerszwer and Petrikaln, *Z. physikal. Chem.*, 1912, **80**, 235; Petrikaln, *Z. Physik*, 1924, **22**, 119; Downey and Emeléus, J., 1924, **125**, 2491; Emeléus and Purcell, *loc. cit.*). Considering first the discharge through phosphorus pentoxide in relation to Johnson's values, the complex band at 3200—3400 Å. is not found in the oxygen spectrum, but at shorter wave-lengths there is close agreement both in the measurements of the main band heads and in their intensities. The last point is well illustrated by the original plates. The oxygen was probably formed by dissociation of the pentoxide. In the glow spectrum none of the bands measured by Johnson in the visible region appears, but, on the other hand, the intense band at 3200—3400 Å. cannot be detected in his plates. At shorter wave-lengths, however, some of the measurements agree with Johnson's, and the general appearance of the two band systems is similar.

The glow spectrum has been produced in other ways which are somewhat difficult to reconcile with the view that it is due to oxygen. For example, it is observed when phosphorus pentoxide is volatilised in the carbon arc or the oxy-hydrogen flame, as well as in the flame of phosphorus. The production of ionised oxygen is, however, thermochemically possible, since the heat evolved in the reaction $2P + \frac{5}{2}O_2 = P_2O_5$ has the remarkably high value of 370 Cal., and the ionisation potential of oxygen is *ca.* 16 volts, which is equivalent to 370 Cal. Little is known of the intermediate reactions leading to the formation of phosphorus pentoxide, but, assuming that a phosphorus pentoxide molecule can transfer its total reaction energy to an oxygen molecule, there is no *à priori* reason why the spectrum of ionised oxygen should not be observed in the arc and flame, as well as in the glow.

Bäckström (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1927, **6**, No. 16) has recently discussed both Stuchtey's work on the thermal decomposition of ozone (*loc. cit.*), and also the oxidation of phosphorus, in the light of a chain-reaction theory of negative catalysis. The luminous oxidation of phosphorus was shown to be accelerated by illumination with a quartz mercury lamp (although the possibility that this effect was due to ozone formation was not considered). This experiment indicated that the oxidation was sensitive to light of the same wave-lengths as it emits, and part of the chemiluminescent light was therefore supposed to be absorbed by molecules of phosphorus (which were shown to absorb light below approx. λ 3000 Å.),

rendering them chemically active, and initiating reaction chains. No assumptions as to the origin of the glow spectrum were, however, involved.

Summarising the present position, our opinion is that the origin of the spectrum of the glow of phosphorus must be regarded as still unsettled, the solution of the problem requiring a more accurate and extensive knowledge of the spectra concerned than is yet available.

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