CXLVIII.—*A Study of the Chemiluminescence of Phosphorus Vapour.*

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THE following work on the luminescence of phosphorus vapour in oxygen was an attempt to compare the number of molecules reacting chemically with the number emitting visible light during the process. The radiation emitted by glowing phosphorus vapour consists of a continuous band extending throughout the visible region (Centnerszwer and Petrikaln, *Z. physikal. Chem.*, 1912, **80**, 235), a band spectrum in the near ultra-violet (Emeléus and Downey, J., 1924, **125**, 2491), and very probably wave-lengths less than 1800 Å. capable of ozonising oxygen. The distribution of energy in these different regions is not known.

The number of molecules producing light during the phosphorescence was determined by measuring photographically the number of quanta of light emitted. One part of a panchromatic plate was exposed to the glow and another part to the light from a tungsten filament lamp passed through a copper sulphate–ferrous sulphate filter to remove infra-red radiation. Equality of blackening on the plate was taken to indicate equality of luminous energy falling on the plate in the two cases. This assumption depends on the similarity of the distribution of energy in the visible region of the spectrum of glowing phosphorus vapour and of the filtered light from the tungsten lamp. It was shown to be justified to a sufficient degree of accuracy by photographs of the two sources of light through glass filters supplied by Messrs. Chance Bros. The following table gives the results :

Transmission region of glass filter (Å.)	7000—5300	6000—4800	4900—4000	3800—3200
Relative blackening for tungsten lamp	4	1	2	0
Relative blackening for phosphorus glow	4	2	1	0

Within a factor of less than 2, equal blackening therefore seemed to indicate equal quantities of energy incident on the plate from the two light sources.

The energy per second in the light from the tungsten lamp was measured with a thermopile calibrated in the usual way with a Hefner lamp. When the panchromatic plate was exposed to the light it was placed much farther away than the thermopile, and the incident energy was calculated by the inverse-square law. The same law was also used, although it is only approximate because of the large size of the light source, in calculating the total luminous energy radiated by the glowing phosphorus vapour from the blackening on the plate placed a known distance away.

In the first series of experiments the white phosphorus was contained in a thin layer, obtained by distillation in a high vacuum, on one half of the inside of a glass bulb about 2 cm. in diameter, which was immersed in water at a suitable temperature. The panchromatic plate was placed a short distance above the bulb. The bulb was connected to a larger bulb to act as a reservoir and to a McLeod gauge. Pure oxygen was admitted to the reservoir and gauge, the initial pressure measured, and the gas allowed to enter the phosphorus bulb. The glow filled the whole bulb, indicating that the reaction was between the oxygen and the phosphorus vapour (Rayleigh, *Proc. Roy. Soc.*, 1924, *A*, **106**, 1). When the reaction had proceeded for a definite time the residual pressure was measured. The glow seemed to remain fairly constant during each experiment, although in different experiments the rate of oxygen absorption varied greatly, apparently depending on the rate of volatilisation of the phosphorus as controlled by variation in a thin crust of oxide on the surface of the solid.

The following are the mean results obtained in three series of experiments :

1. Initial oxygen pressure = 5·17 mm.

Blackening on plate by phosphorus glow corresponds (from tungsten lamp–thermopile calibration) to $1{\cdot}76 \times 10^{-6}$ cal. per sq. cm.

Fraction of glow received on 1 sq. cm. of plate = $1/16\pi$ (approx.). Therefore total luminous energy emitted as phosphorescence = $8{\cdot}85 \times 10^{-5}$ cal.

If $h\nu = 8{\cdot}3 \times 10^{-20}$ cal. be taken as a mean energy of a quantum in the visible region, number of quanta emitted during the glow = $1{\cdot}06 \times 10^{15}$.

Number of molecules of oxygen absorbed

$$= 6 \times 10^{23} \times (\text{vol. of apparatus})(\text{cm. } O_2 \text{ absorbed})/76 \times 23{,}000$$
$$= 3{\cdot}42 \times 10^{19}.$$

The final product of oxidation is phosphoric oxide, produced as a result of a series of consecutive reactions; of these we may assume that only one emits light, and that it probably involves only one molecule of oxygen. If this is so, one-fifth of the oxygen molecules reacting may be taken as the number concerned in the luminescent stage.

If r represents the ratio of the number of such molecules to the number of quanta of light emitted, we have

$$r = 6{\cdot}8 \times 10^{18}/1{\cdot}06 \times 10^{15} = 6{\cdot}4 \times 10^{3}.$$

2. Initial oxygen pressure = 3·5 mm.
Number of quanta emitted during the glow = 4×10^{14}.
Total number of molecules of O_2 absorbed = $3{\cdot}4 \times 10^{19}$.

$$r = 6{\cdot}8 \times 10^{18}/4 \times 10^{14} = 1{\cdot}7 \times 10^{4}.$$

3. Initial oxygen pressure = 1·18 mm.
Number of quanta emitted during the glow = $1{\cdot}42 \times 10^{15}$.
Total number of molecules of O_2 absorbed = $2{\cdot}4 \times 10^{19}$.

$$r = 4{\cdot}8 \times 10^{18}/1{\cdot}42 \times 10^{15} = 3{\cdot}4 \times 10^{3}.$$

An important source of error in these experiments was the possible reaction of some of the oxygen with the solid phosphorus present, *i.e.*, the combination might not take place wholly in the vapour phase. To eliminate this, another series of experiments was performed. Phosphorus was vaporised at about 25° in a current of pure dry nitrogen and the gas passed into a small warmed bulb into which oxygen was allowed to leak. The glow in the vessel was photographed as before. To secure greater accuracy of comparison a neutral optical wedge was used in front of the plate for the exposure to the calibrated lamp, the times of exposure to the glow and to the lamp being the same. The amount of oxygen reacting with the phosphorus vapour was found by drawing the gases into a small vessel cooled in carbonic acid snow, and weighing the oxide deposited. The results of four experiments are given below :

Energy from lamp = $2{\cdot}5 \times 10^{-6}$ cal. per sec. per sq. cm. of plate.
Fraction of glow received on 1 sq. cm. of plate = 0·05.

Ratio of energy : glow/lamp.	Quanta emitted as luminescence per sec.	P_4O_{10} collected in 30 mins. (g.).	Molecules produced per sec.	Ratio Mols./Quanta.
1/10	6×10^{13}	0·121	$13{\cdot}1 \times 10^{16}$	$2{\cdot}18 \times 10^{3}$
1/8	$7{\cdot}5 \times 10^{13}$	0·126	$13{\cdot}6 \times 10^{16}$	$1{\cdot}81 \times 10^{3}$
1/10	6×10^{13}	0·129	$13{\cdot}9 \times 10^{16}$	$2{\cdot}32 \times 10^{3}$
1/12	$5{\cdot}2 \times 10^{13}$	0·121	$13{\cdot}1 \times 10^{16}$	$2{\cdot}52 \times 10^{3}$

These results are in agreement with those obtained by the previous method, and indicate that at least one in 2000 of the P_4 molecules undergoing oxidation emits a quantum of visible light. The agreement between the two series of experiments, however, must be viewed in the light of the assumptions made in the first series and of the possible effect of nitrogen on the glow in the second. As the light emitted is partly obscured by the cloud of solid oxide formed, the proportion of luminescent molecules is probably greater; also the number of molecules emitting ultra-violet light is not given by these experiments. Rayleigh (*loc. cit.*) has shown that the oxidation of phosphorus vapour with luminescence is a catalytic phenomenon occurring at the surface of solid oxide particles. The results of this paper on the fairly large proportion of luminescent molecules in the oxidation, when account is taken of the losses of light and of ultra-violet light emitted, seem to be most simply interpreted by assuming that the glow of phosphorus is a chemiluminescence of the type described by Kautsky (*Trans. Faraday Soc.*, 1926, **21**, 591). In his experiments, dyes adsorbed on a surface of siloxen undergoing oxidation were excited to emit their fluorescent spectrum as chemiluminescence. If the theory is extended to the case of phosphorus, it must be assumed that oxidation at the surface of solid particles of an oxide excites to luminescence adsorbed molecules of some other oxide. A large number of chemiluminescence phenomena are associated with reactions on solid particles, two well-defined cases being the oxidation of phosphorus and the oxidation of the dithiocarbonic acid esters. The curious phenomenon of the glow and explosion of so-called pure phosphine and oxygen mixtures when the pressure is suddenly reduced (van 't Hoff, " Studies in Chemical Dynamics," 1896), which has been shown by Emeléus (J., 1925, **127**, 1362) to emit the spectrum of glowing phosphorus, can only be reasonably explained by the catalytic effect of solid hydrogen phosphides or other particles deposited by the sudden cooling.

An interesting calculation is the " efficiency " of the oxidation of phosphorus as a light producer. The heat of formation of 1 g.-mol. of P_4O_{10} is 740,000 cals. A g.-mol. quantum of green light is 50,000 cals., whence, during phosphorescence,

$$\text{Energy of light/Total energy} = 3 \times 10^{-5}.$$

This is not a very high efficiency when compared with that for a candle, 10^{-2}; an electric lamp, 10^{-1}; or a mercury-vapour lamp, 0·5.

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