

**286.** *The Chain Theory of the Oxidation of Phosphorus Vapour. Part I. Comparison of the Effect of Hydrogen, Deuterium, and Helium on the Lower Explosion Limit of Phosphorus-Oxygen Mixtures. Part II. Displacement of the Lower Limit by Ultra-violet Light. Part III. Influence of Ultra-violet Light on the Upper Limit. Part IV. The Stable Oxidation Reaction below the Lower Limit. Part V. The Transformation of White into Red Phosphorus by Means of Ultra-violet Light.*

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I. Deuterium and helium are almost equal in their efficiency in preventing the explosion chain carriers reaching the walls, and hydrogen is less efficient, the efficiencies being in the ratio  $H_2 : D_2 : He = 1 : 1.30 : 1.32$ .

II. Illumination below the lower limit produced two effects: (a) displacement of the lower limit towards smaller pressures, (b) reaction between phosphorus and oxygen below the lower limit. The displacement is not permanent, but slowly decays if the reaction mixture is allowed to stand before being exploded. The displacement is a wall effect, probably due in the first place to dissociation of  $P_4$  into  $P_3$ .

III. Illumination resulted in a raising of the upper limit. This could not be a wall effect and is probably due to the production of  $P_3$  molecules.

IV. The rate of the stable reaction was found to be proportional to the pressure of  $P_4$  and to the square of the oxygen pressure, but independent of the pressure of inert gas.

V. The rate of transformation of  $P_4$  into red phosphorus was found to follow a unimolecular law.

PART I. COMPARISON OF THE EFFECT OF HYDROGEN, DEUTERIUM, AND HELIUM ON THE LOWER EXPLOSION LIMIT OF PHOSPHORUS-OXYGEN MIXTURES.

THE existence of an upper limiting pressure of oxygen for a given pressure of phosphorus, above which there is no appreciable reaction, was discovered by Berthollet in 1797. The discovery that there was also a lower limit below which no reaction could be observed was made by Joubert [*Ann. Sci. Ecole norm.*, 1874, Suppl. (2), 3, 207] about 80 years later. Between these two limits phosphorus vapour and oxygen inflame. No satisfactory explanation of the existence of the limits was given by their discoverers.

Chariton and Walta (*Z. Physik*, 1926, 39, 547) showed that by the addition of argon to a  $P_4$ -oxygen mixture, inflammation could be provoked at lower pressures than in its absence. These experiments were repeated and confirmed by Semenov (*ibid.*, 1927, 46, 109; 1928, 48, 511), who also showed that the lower limit could be defined by the equation

$$p_{P_4}^2 p_{O_2} [1 + p_X / (p_{O_2} + p_{P_4})] a^2 = \text{constant} \quad . \quad . \quad . \quad (1)$$

where  $d$  was the diameter of the vessel, and  $p_P$ ,  $p_O$ ,  $p_X$  were respectively the pressures of phosphorus vapour, oxygen, and inert gas at the lower limit.

From these experiments, Semenoff (*Z. physikal. Chem.*, 1928, *B*, **2**, 161; *Chem. Reviews*, 1929, **6**, 343) was able to develop a quantitative treatment of the reaction in terms of the chain theory. He suggested that the oxidation of phosphorus was a chain reaction in which the chain carriers were oxygen atoms and phosphorus oxide molecules, the chains being broken at the lower limit by adsorption of the carriers on the walls of the containing vessel. These chains were also supposed to be branching chains, the upper and lower limits being at that point where the rate of branching just balanced the rate of deactivation of the chain carriers—in the gas phase for the upper limit, and at the walls for the lower one. By use of the general equations characterising chain reactions, Semenoff obtained an expression for the lower limit almost identical with that obtained from experimental results, *viz.*,

$$p_P p_O [1 + p_X / (p_P + p_O)] d^2 = \text{constant} \quad . \quad . \quad . \quad (2)$$

In deriving this expression, he made several assumptions which, viewed in relation to the knowledge of the processes whereby excited atoms and molecules can lose their energy, are scarcely satisfactory. Moreover, he assumed a definite mechanism for the propagation of the chains in the gas phase. The initial centres are supposed to be oxygen atoms which, combining with phosphorus molecules, form intermediate active molecules of  $P_4O$ ; these molecules on combining with oxygen molecules form  $P_4O_2$  and regenerate free oxygen atoms again, so Semenoff's scheme for the development of the primary reaction is



Sufficient amounts of energy are liberated in the oxidation of  $P_4O_2$  to  $P_4O_{10}$  to guarantee the secondary dissociation of the oxygen molecule into its two atoms, so enabling the reaction chains to branch. Rupture of the reaction chains is due to adsorption of the oxygen atoms by the walls.

A more satisfactory method of obtaining equation (2) was given by Dalton and Hinshelwood (*Proc. Roy. Soc.*, 1929, *A*, **125**, 290), who made no assumption of a definite mechanism for the reaction.

Melville and Ludlam (*ibid.*, 1931, *A*, **132**, 108) carried out a series of experiments at the lower limit, using 14 different inert gases, and showed that Semenoff's equation was valid provided that the concentration of the inert gas  $p_X$  was multiplied by some additional factor  $\mu$ , which was inversely proportional to the diffusion coefficient of the chain carriers into the inert gas present. Semenoff's equation was therefore modified to

$$p_P p_O [1 + \mu p_X / (p_P + p_O)] = \text{constant (for a given tube)} \quad . \quad . \quad . \quad (3)$$

Investigation of the theoretical basis for this empirical change was extremely difficult, since the rate of diffusion of the reaction chain involves the diffusion of two chain propagators, which alternately appear and disappear in the development of the chain, in a ternary mixture. Semenoff (*Z. physikal. Chem.*, 1929, *B*, **2**, 161) attempted a rigorous and exact solution of the problem for the hydrogen-oxygen reaction, in which he assumed that the chain propagators were hydrogen atoms and  $HO_2$  molecules. According to Gray and Melville (*Trans. Faraday Soc.*, 1935, **31**, 452), a simpler treatment of the problem can be obtained if it is assumed that the chain carriers have the same diameters and masses. They showed that the value of  $\mu_X$ , the inert-gas factor, is given by:

$$\mu_X = \sigma_{AX}^2 \left( \frac{1}{M_A} + \frac{1}{M_M} \right)^{\frac{1}{2}} / \sigma_{AM}^2 \left( \frac{1}{M_A} + \frac{1}{M_X} \right)^{\frac{1}{2}} \quad . \quad . \quad . \quad (4)$$

where  $\sigma_{AX}$  is the sum of the molecular radii of the chain carrier A and the inert gas X;  $\sigma_{AM}$  is the sum of the molecular radii of A and M, the mean value for the reactant gases ( $P_4$ ,  $O_2$ );  $M_M$  is the mean molecular weight of the reactants, and  $M_X$  and  $M_A$  are the molecular weights of the inert gas and of the chain carriers respectively. It is seen that the factor by which  $p_X$  is multiplied is not the diffusion coefficient (it is proportional to it),

but a factor expressing the molecular weight and molecular diameter of the inert gas molecules and the chain carriers. It seemed, therefore, useful to investigate and compare the inert-gas effect obtained by using hydrogen, deuterium, and helium, with a view to confirm the above expression, and also to complete the work on the effect of foreign gases on the lower critical oxidation limit.

Now if  $M_A$  is large in comparison with  $M_X$ ,  $1/M_A$  may be neglected. The chain carriers in the phosphorus-oxygen reaction are assumed to be either an oxygen atom or an activated oxygen molecule and some lower oxide of phosphorus of the type  $P_4O_n$ , so that in comparison with the molecular weight of hydrogen, deuterium, and helium,  $1/M_A$  may be neglected as a close approximation. Also,  $1/M_A + 1/M_M$  and  $\sigma_{AM}$  remain constant for this reaction, so (4) becomes

$$\mu_X = k_1 \sigma_{AX}^2 / k_2 (1/M_X)^{\frac{1}{2}} \quad (5)$$

where  $k_1 = (1/M_A + 1/M_M)^{\frac{1}{2}}$  and  $k_2 = \sigma_{AM}$ .

Hydrogen and deuterium have been shown to have the same molecular diameters (van Cleave and Maass, *Canad. J. Res.*, 1935, **12**, 57; Farkas and Farkas, *Naturwiss.*, 1934, **22**, 218), so that, from the point of view of the inert-gas effect, they differ only in the fact that deuterium has twice the mass of hydrogen. Hence, from (5),  $\mu_{H_2}/\mu_{D_2} = 1/\sqrt{2}$ . Helium, although possessing the same mass as deuterium, has been shown to have a slightly larger molecular diameter than hydrogen, and hence than deuterium, so that  $\mu_{D_2}/\mu_{He} = \sigma_{AD}^2/\sigma_{AHe}^2$ . Any difference between the experimental values of  $\mu_{D_2}$  and  $\mu_{He}$  must be ascribed therefore to the difference in molecular diameter; so it was interesting to see whether this small difference was sufficient to cause any appreciable difference in the corresponding values of  $\mu$ .

The apparatus need not be described in detail, for it closely resembled that of Melville and Ludlam (*loc. cit.*). The reaction vessel was a silica bulb, as it was also used for investigating the action of ultra-violet light on the oxidation. The deuterium was prepared from heavy water containing 99.95%  $D_2O$ .

Typical sets of results are given in Table I, in which all pressures are in mm. of mercury. The temperature of the reaction vessel was 15°, and that of the phosphorus reservoir 0°, in all three cases.

TABLE I.

Hydrogen.				Deuterium.				Helium.			
$p_X$ .	$p_{O_2}$ .	$\frac{1}{p_{O_2}}$ .	$\frac{p_X}{p_{O_2} + p_{P_4}}$ .	$p_X$ .	$p_{O_2}$ .	$\frac{1}{p_{O_2}}$ .	$\frac{p_X}{p_{O_2} + p_{P_4}}$ .	$p_X$ .	$p_{O_2}$ .	$\frac{1}{p_{O_2}}$ .	$\frac{p_X}{p_{O_2} + p_{P_4}}$ .
0	0.0208	48.0	0	0	0.0208	48.0	0	0	0.0208	48.0	0
0.0232	0.0191	52.3	1.0	0.0198	0.0189	52.9	0.9	0.0161	0.0190	53.0	0.8
0.0232	0.0191	52.3	1.0	0.0198	0.0195	51.3	0.8	0.0161	0.0196	51.0	0.7
0.0480	0.0175	57.1	2.1	0.0390	0.0161	62.3	1.9	0.0315	0.0178	56.2	1.4
0.0460	0.0179	55.9	2.1	0.0390	0.0166	60.2	1.9	0.0321	0.0172	58.1	1.5
0.0680	0.0154	64.9	3.5	0.0591	0.0144	69.5	3.2	0.0470	0.0156	64.1	2.4
0.0680	0.0150	66.7	3.6	0.0596	0.0147	67.9	3.2	0.0470	0.0156	64.1	2.4
0.0692	0.0159	62.7	3.5	0.0764	0.0132	75.7	4.5	0.0626	0.0141	70.8	3.4
0.0914	0.0136	73.6	5.1	0.0782	0.0128	78.1	4.7	0.0620	0.0139	72.1	3.6
0.0910	0.0143	69.9	5.0	0.0986	0.0117	85.5	6.3	0.0786	0.0132	75.8	4.6
0.0120	0.0126	79.3	6.7	0.0986	0.0117	85.5	6.3	0.0780	0.0129	77.5	4.6
0.0120	0.0126	79.3	6.7	0.1119	0.0107	93.5	7.6	0.0946	0.0118	84.7	6.0
0.1342	0.0108	92.6	9.1	0.1108	0.0109	91.8	7.4	0.0954	0.0122	82.0	5.9
0.1342	0.0111	90.2	8.9	0.1275	0.0100	100	9.1	0.1095	0.0106	94.3	7.5
0.1574	0.0104	96.1	10.9	0.1275	0.0092	109	9.6	0.1100	0.0106	94.3	7.3
0.1568	0.0100	100.0	11.2	0.1376	0.0089	112	10.7	0.1246	0.0092	109	9.4
0.1811	0.0090	111	14.0	0.1380	0.0088	114	10.8	0.1250	0.0095	105	9.2
0.1820	0.0088	114	14.2	0	0.0208	48.0	0	0.1413	0.0084	119	11.4
0	0.0208	48.0	0					0	0.0208	48.0	0

The results are summarised in Fig. 1, where the reciprocal of the critical oxygen pressure  $p_{O_2}$  is plotted against the quantity  $p_X/(p_{P_4} + p_{O_2})$  for the three inert gases, hydrogen, helium, and deuterium. It is seen that helium is only very slightly more effective than deuterium, but both have a much greater effect than hydrogen. From the slopes of the

curves in Fig. 1 it was found that the ratio of the values of the inert-gas factor  $\mu$  for the three gases was given by  $\mu_{\text{H}_2} : \mu_{\text{D}_2} : \mu_{\text{He}} = 1.00 : 1.30 : 1.32$ . The slope of the curve for hydrogen is nearer that for helium and deuterium than would be expected at first sight from theoretical considerations. However, if the number of assumptions and approximations made in deriving the expression for the inert-gas factor  $\mu_x$  [equation (4)] is considered, these values obtained for  $\mu_{\text{H}_2}$ ,  $\mu_{\text{D}_2}$ , and  $\mu_{\text{He}}$  are quite within reason. The difficulty in deriving theoretically an expression for  $\mu$  for an inert gas has been explained on p. 1501. A rigorous solution of the problem is probably impossible, and would give rise to a very complicated expression containing a number of immeasurable factors.

In deriving and in using the theoretical expression (4) for the inert-gas factor, certain variations and assumptions had to be made owing to the difficulty in knowing the nature and the physical constants of the two chain carriers. Semenov (*Z. Physik*, 1927, **47**, 109) assumes that one of the chain carriers is an oxygen atom (or, less likely, an activated oxygen molecule; Childe and Mecke, *ibid.*, 1931, **68**, 344) and the other some lower oxide of phosphorus of the type  $\text{P}_4\text{O}_n$ . If this view is correct, then  $M_A$  will have a minimum value of roughly 70, so the neglect of  $1/M_A$  in comparison with  $1/M_x$  (see p. 1502) is justified.

The theoretical value for  $\mu_{\text{D}_2}/\mu_{\text{H}_2}$ , viz.,  $\sqrt{2}$ , is somewhat higher than that found experimentally. However, it has been suggested from results obtained by Melville and Ludlam (*Proc. Roy. Soc., A*, 1932, **135**, 315) in experiments carried out with a tungsten filament, that the rate of starting of chains in the phosphorus-oxygen reaction may be proportional to  $p_{\text{P}_2}^{\frac{1}{2}}$ , a suggestion which indicates the possibility of  $\text{P}_2$  molecules playing some essential part in the initial stages of the reaction. Evidence in favour of this view has been obtained by projecting a beam of  $\text{P}_2$  molecules (Melville, Thesis, Edinburgh, 1932; Preuner and Brockmüller, *Z. physikal. Chem.*, 1912, **81**, 159) into oxygen, whereupon the typical glow emitted from a phosphorus-oxygen explosion was observed. Although the evidence that  $\text{P}_2$  molecules play an important rôle as chain carriers in the oxidation of phosphorus is not very strong, and is open to the serious objection that either one of the chain carriers may be produced in some way by the reaction of the  $\text{P}_2$  molecules with oxygen or  $\text{P}_4$  molecules which then results in the initiation and development of the chains, yet it is possible that one of the chain carriers is a  $\text{P}_2$  molecule. In the event of this being true,  $M_A$  would have a value of approximately 35, so that  $1/M_A$  could not be neglected as before, and  $\mu_{\text{D}_2}/\mu_{\text{H}_2}$  would have a smaller value than  $\sqrt{2}$ , although not so low as to account fully for the experimental results.

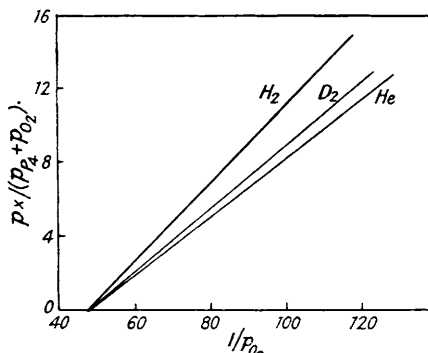
## PART II. DISPLACEMENT OF THE LOWER LIMIT BY ULTRA-VIOLET LIGHT.

It is assumed in the derivation of expressions for the explosion limit that this should be independent of the rate of starting of the chains, provided, of course, that some reaction, even although too small to be measured, does take place. The stationary concentration of one of the chain carriers  $\text{X}_0$  in the phosphorus-oxygen reaction is given by

$$[\text{X}_0] = \frac{k_1 k_2 [\text{O}_2] F(c) + k_1 K F(c)}{(1 - \alpha) k_2 k_3 [\text{P}_4] [\text{O}_2] + k_2 K [\text{O}_2] + k_3 K [\text{P}_4] + K^2} \quad (6)$$

where  $k_1$ ,  $k_2$ , and  $k_3$  are velocity coefficients,  $[\text{O}_2]$  and  $[\text{P}_4]$  concentrations of oxygen and phosphorus vapour respectively, and  $K$  the rate of deactivation of  $\text{X}_0$  at the walls;  $k_1 F(c)$  is the initial rate of production of the chain centres, and  $\alpha$  introduces the condition that more than one molecule of  $\text{X}_0$  can be produced from the other chain carrier  $\text{X}_p$  at col-

FIG. 1.



Effect of hydrogen, deuterium, and helium in preventing chain carriers reaching the walls (least for hydrogen).

losion, *i.e.*, branching can take place. At explosion, however,  $[X_o]$  will be infinitely great, so the condition for explosion is that

$$(1 - \alpha)k_2k_3[P_4][O_2] + k_2K[O_2] + k_3K[P_4] + K^2 = 0 \quad . \quad . \quad (7)$$

As the term  $F(c)$  does not appear in the denominator, it follows that the explosion limits should be independent of the rate of production of the chain centres. This critical explosion pressure may be either an upper or a lower limit, depending on whether the chains are broken by deactivation of the chain carriers in the gas phase or at the walls. At low pressures, deactivation takes place almost entirely at the walls, so that if, on increasing the pressure, the rate of production of new chains owing to the occurrence of branching may equal or exceed the rate of deactivation, then a sharp change from a slow or non-detectable reaction to an explosive one may occur. This gives rise to a lower limit. As the pressure is still further increased, deactivation of the carriers by collision in the gas phase becomes a more prominent factor, until finally, wall deactivation becomes negligible. Thus, on increasing the pressure it may be possible to reach a state where deactivation of the carriers in the gas phase equals or exceeds the rate of branching, so that the reaction ceases to become an explosive reaction, giving rise to an upper explosion limit.

Now there is ample evidence that, apart from the oxidation of phosphorus and of phosphine, the position of both explosion limits is dependent on the rate at which the chains are started. Hydrogen atoms, produced photochemically (Farkas, Haber, and Harteck, *Z. Elektrochem.*, 1930, **36**, 711; Taylor and Salley, *J. Amer. Chem. Soc.*, 1933, **55**, 96), thermally (Haber and Oppenheimer, *Z. physikal. Chem.*, 1932, *B*, **16**, 443), or electrically (Semenoff, *Trans. Faraday Soc.*, 1933, **29**, 606), oxygen atoms, and chlorine atoms (Norrish, *Proc. Roy. Soc.*, 1931, *A*, **135**, 334) all reduce the temperature of spontaneous ignition of hydrogen-oxygen mixtures, and at temperatures approximating to room temperature, conditions simulating a lower explosion pressure can be obtained by using a spark to start the chains (Thompson, *Trans. Faraday Soc.*, 1932, **28**, 308). Other examples of the displacement of the position of explosion limits, owing to their partial dependence on the rate of production of chain centres, are afforded by the reduction in ignition temperature of hydrogen, carbon monoxide, and methane by nitrogen peroxide. A similar alteration in the explosion limits in the oxidation of carbon disulphide (Semenoff and Rjabin, *Z. physikal. Chem.*, 1928, *B*, **1**, 192), sulphur (Ritchie, *Proc. Roy. Soc.*, 1932, *A*, **137**, 511), and hydrogen sulphide can be obtained by the use of suitable stimuli.

These reactions, however, have two properties in common which are not shown in the oxidation of phosphorus and phosphine, *viz.*, that their explosion limits are influenced by temperature changes and that explosion takes place at fairly high temperatures. The situation may be summarised by the statement that in those chain reactions where the explosion limits are temperature-dependent, and explosion takes place at high temperatures, the chain hypothesis does not entirely express the condition for explosion, since the position of both explosion limits is partly dependent on the rate of initiation. Hence, to express completely the condition for explosion, some temperature-dependent factor should be introduced.

With phosphorus and phosphine, however, the propagating collisions are almost 100% efficient, so the efficiency is for all practical purposes independent of the temperature. In addition to this, the termination reactions at the walls or in the gas phase are independent of temperature, so it is to be expected that the pure chain explosion would occur in these cases. If so, the condition for explosion would be adequately expressed by the statement that the product of the probabilities of branching and of termination of the chains is equal to unity. Consequently, the explosion pressure should be quite independent of the rate of starting of the chains. Hence, by introducing active centres into phosphorus-oxygen mixtures and examining the effect on the explosion limits, it should be possible to prove or disprove the above statement, incidentally putting some parts of the chain theory to a somewhat crucial test. This test was applied to the explosion limits of phosphine, and a displacement of both limits occurred (Clusius and Hinshelwood, *ibid.*, 1930, *A*, **129**, 589; Melville and Roxburgh, *J. Chem. Physics*, 1932,

2, 739). Melville, however, showed that the displacement of the lower limit was due to a change in the condition of the walls (*Proc. Roy. Soc., 1932, A, 138, 389*).

Semenoff, in his quantitative development of the chain theory, has shown that the velocity of the stable reaction is given by

$$W = n_0 / (1 - \alpha) \dots \dots \dots (8)$$

where  $n_0$  is the number of initial centres, and  $\alpha$  the average number of elementary reactions entailed by one given reaction, *i.e.*, the probability of the continuation of the chain. It was possible, therefore, that the introduction of further active centres into the phosphorus-oxygen mixture would result in a sufficient increase in  $n_0$  to produce a measurable stable reaction below the lower explosion limit. Of the two easily controllable methods of introducing active molecules into a gaseous mixture without raising the temperature, *i.e.*, by a filament or photochemically, it was decided to use the latter, in the hope of testing the statement that the explosion limits should be independent of the rate of initiation of chains.

Photographs of the absorption spectrum of phosphorus vapour, taken with the continuous spectrum of a water-cooled hydrogen discharge tube, showed that the absorption was continuous, and was ample for our purpose at wave-lengths longer than those at which oxygen absorption commenced, even down to the mercury line at  $\lambda 2537$ ; hence, either a zinc spark or a mercury-vapour lamp could be used as the source of illumination.

The apparatus did not differ in any important respect from that used in previous work. The explosion vessel was a bulb of silica in which the phosphorus was contained at a known pressure. The oxygen entered through a capillary, and preliminary determination of the rate of flow gave the pressure the gas attained in an observed time. The time,  $t_1$ , necessary for explosion to take place in the dark was noted, the vessel was pumped out, refilled with phosphorus vapour, and oxygen allowed to enter for a time  $t_2$ , less than  $t_1$ ; the mixture was illuminated for the desired length of time,  $T$ , the flow of oxygen was restarted, and the time,  $t_3$ , noted for the explosion to occur. Therefore  $t_1 - (t_2 + t_3)$ , the difference between the oxygen pressure for explosion to occur in a non-illuminated and in an illuminated mixture, gave a measure of the effect of the illumination.

*Results.*—Table II shows a typical set of results obtained in the preliminary investigation, during which mixtures of phosphorus vapour and oxygen, containing the same pressures of both, were illuminated with light from the zinc spark for different periods of time,  $T$ . In Fig. 2 the total pressure of oxygen (measured in terms of  $t_1 + t_2$ ) is plotted against period of illumination.

FIG. 2.

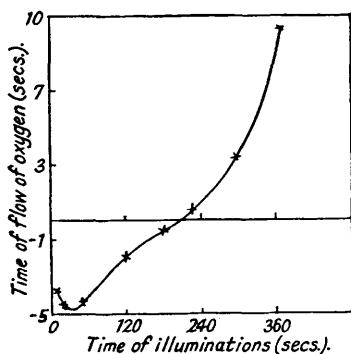
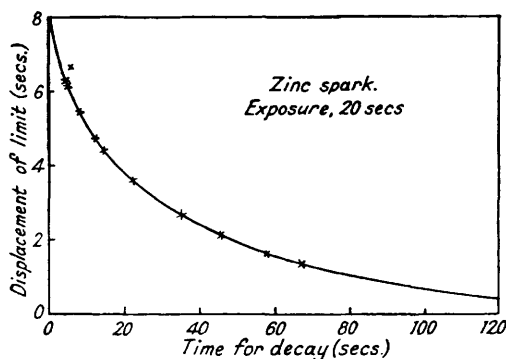


FIG. 3



The last column of Table II shows  $t_1 - (t_2 + t_3)$ . From Fig. 2, it is seen that for exposures of 180 secs. and less, the total pressure of oxygen required for explosion was less than the normal explosion pressure of a similar mixture. Evidently, the mixture on illumination had become more susceptible to explosion, thus resulting in a lowering of the critical pressure. For longer exposures than 180 secs., the total pressure of oxygen required for explosion was greater than for a non-illuminated mixture. It was evident, therefore, that besides displacing the lower limit, illumination resulted in the production of a stable reaction below the lower

limit. By altering the intensity and length of illumination, it was possible to eliminate the latter phenomenon and so investigate the displacement of the lower limit.

During the following series of experiments, the length of exposure of the phosphorus-oxygen mixtures to ultra-violet light was reduced to 15 secs., and the intensity of light reduced so that very little photo-oxidation occurred. The actual experimental procedure differed very little from that in the previous experiment.

TABLE II.

Zinc spark.		Temp. of phosphorus reservoir, 0°.			Temp. of reaction vessel, 16°.				
From calibration curve: 1 sec. = $3.86 \times 10^{-4}$ mm. Hg.									
<i>T</i> (secs.).	Initial concn. of O <sub>2</sub> , <i>t</i> <sub>1</sub> (secs.).	Time for ex- plosion, <i>t</i> <sub>2</sub> (secs.).	Total press. of O <sub>2</sub> , ( <i>t</i> <sub>1</sub> + <i>t</i> <sub>2</sub> ), secs.	Amount of O <sub>2</sub> used (secs.).	<i>T</i> (secs.).	Initial concn. of O <sub>2</sub> , <i>t</i> <sub>1</sub> (secs.).	Time for ex- plosion, <i>t</i> <sub>2</sub> (secs.).	Total press. of O <sub>2</sub> , ( <i>t</i> <sub>1</sub> + <i>t</i> <sub>2</sub> ), secs.	Amount of O <sub>2</sub> used (secs.).
0	0	98.8	98.8	—	60	82.5	11.9	94.4	— 4.4
360	82.5	26.9	109.4	10.6	30	82.5	11.3	93.8	— 5.0
300	82.5	19.6	102.1	3.3	20	82.5	11.4	93.9	— 4.9
240	82.5	17.0	99.5	0.7	10	82.5	12.4	94.9	— 3.9
180	82.5	15.7	98.2	-0.6	1200	82.5	45.2	127.7	+28.9
120	82.5	14.2	96.7	-2.1	0	0	98.8	98.8	—

Phosphorus vapour was admitted into the reaction vessel, and oxygen allowed to enter until it had nearly reached the explosion limit, the flow being then stopped and the mixture illuminated for 15 secs. The flow of oxygen was restarted, and the time for explosion noted.

Different intervals of time (*t*) were allowed to elapse between the cessation of illumination and the occurrence of explosion, so that the persistence of the effect could be determined. By plotting the time allowed for decay (*t*) against amount of lowering of the explosion limit, a decay curve was obtained (Fig. 3).

In later experiments the zinc spark was replaced by a mercury-vapour lamp, which was more suitable for the work. Care was taken to exclude all mercury vapour from the reaction vessel, by means of a liquid-air trap between it and the McLeod gauge, so that no photosensitisation could take place. Tables III and IV respectively show the results obtained by illuminating the phosphorus-oxygen mixtures with light from the zinc spark and from the mercury arc. The pressures of oxygen are expressed in seconds.

TABLE III.

Zinc spark.		Exposure, 20 secs.		Temp. of phosphorus, 0°.			
From calibration curve: 1 sec. = $7.1 \times 10^{-4}$ mm. Hg.							
Explosion press. (secs.).	Time for decay, <i>t</i> (secs.).	Explosion press. (secs.) after illumtn.	Lowering of limit after <i>t</i> secs.	Explosion press. (secs.).	Time for decay, <i>t</i> (secs.).	Explosion press. (secs.) after illumtn.	Lowering of limit after <i>t</i> secs.
70.3	65.8	68.8	1.5	70.4	9.5	65.0	5.4
70.6	55.0	68.1	2.5	70.9	6.6	64.3	6.6
69.2	46.3	69.9	2.3	70.5	26.9	67.1	3.4
69.6	36.0	66.7	2.9	71.0	37.8	68.1	2.9
70.5	27.0	67.1	3.4	71.2	48.4	68.7	2.5
70.8	16.8	66.6	4.2	70.8	58.9	68.9	1.9
70.8	5.1	64.8	6.0	71.0	66.7	69.7	1.3
70.5	4.5	64.4	6.1	70.9	66.9	69.9	1.0

In Table IV the results marked A were obtained in a clean reaction vessel, whereas those marked B were obtained after the vessel had been in use for some time. From the decay curves it was evident that the rate of decay was influenced to some extent by the condition of the walls of the containing vessel.

Other series of experiments are given in Table V, where the length of exposure and pressure of phosphorus vapour were kept constant, whilst the pressure of oxygen varied from zero to just below the explosion pressure. It was necessary to find the effect of varying the oxygen pressure on the rate of decay in view of the future investigation of the stable oxidation reaction below the lower limit. These experiments were carried out in a different reaction vessel from that used in the preliminary investigation.

TABLE IV.

Mercury arc. Exposure, 15 secs. Temp. of phosphorus, 0°.  
From calibration curve: 1 sec. =  $6.9 \times 10^{-4}$  mm. Hg.

	Normal explosion press. ( $T_0$ secs.).	Time for decay ( $t$ secs.).	Initial concn. of $O_2$ ( $T_1$ secs.).	Time for explosion ( $T_2$ secs.).	Lowering of limit, $T_0 - (T_1 + T_2)$ .
A	72.2	6.7	60.2	4.1	7.9
	72.2	6.8	60.2	4.3	7.7
	72.3	18.2	60.2	5.8	6.3
	72.5	29.7	60.2	7.3	5.0
	72.5	52.4	60.2	9.6	2.7
	72.1	83.5	60.2	10.9	1.0
	72.2	104	60.2	11.8	0.2
	72.2	150	60.2	12.0	0
72.2	201	60.2	12.0	0	
B	73.3	5.7	60.2	3.6	9.5
	73.1	17.4	60.2	5.4	7.5
	73.3	28.9	60.2	6.7	6.4
	73.3	51.0	60.2	8.7	4.4
	73.1	82.9	60.2	10.8	2.1
	73.2	104	60.2	11.7	1.3
	72.9	145	60.2	12.6	0.1
	73.0	315	60.2	12.8	0

TABLE V.

Mercury arc. Exposure, 15 secs. Temp. of phosphorus, 0°.  
From calibration curve: 1 sec. =  $5.78 \times 10^{-4}$  mm. Hg.

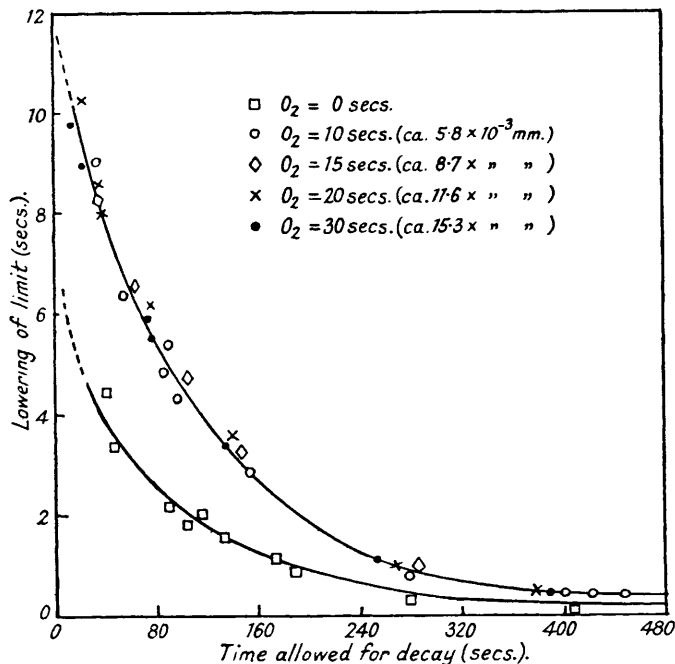
Initl. [ $O_2$ ] (secs.).	Time for expln. (secs.).	Total $O_2$ required for expln.	Displmt. of lower limit (secs.).	Time for decay (secs.).	Initl. [ $O_2$ ] (secs.).	Time for expln. (secs.).	Total $O_2$ required for expln.	Displmt. of lower limit (secs.).	Time for decay (secs.).
0	47.6	47.6	—	—	10.0	37.5	47.5	—	—
0	44.2	44.2	3.4	45	10.3	32.7	43.0	4.5	90
0	45.3	45.3	2.3	86	10.2	28.2	38.4	9.1	30
0	45.9	45.9	1.7	127	10.4	30.9	41.3	6.2	62
0	46.4	46.4	1.2	168	10.4	32.3	42.7	4.8	93
0	46.9	46.9	0.7	289	10.2	34.5	44.7	2.8	156
0	47.3	47.3	0.3	450	10.2	36.7	46.9	0.6	279
0	43.0	43.0	4.6	43	10.2	36.9	47.1	0.4	398
0	45.6	45.6	2.0	76	10.0	37.5	47.5	—	—
0	45.3	45.3	2.3	115	15.0	32.5	47.5	—	—
0	46.7	46.7	0.9	189	15.1	24.1	39.2	8.3	34
0	47.5	47.5	0.1	284	15.0	24.6	39.6	7.9	40
0	47.4	47.4	0.2	404	15.0	26.1	41.1	6.4	61
0	47.6	47.6	—	—	15.0	27.1	42.1	5.4	90
					15.3	28.9	44.2	3.3	145
30.4	17.9	48.3	—	—	15.3	29.9	45.2	2.3	205
30.4	8.1	38.5	9.8	8.1	15.0	31.6	46.6	0.9	327
30.3	8.9	39.2	9.1	22	15.3	31.8	47.1	0.4	420
35.0	5.0	40.0	8.3	15	15.2	32.3	47.5	—	—
35.0	5.4	40.4	7.9	25	20.2	27.5	47.7	—	—
30.4	9.1	39.5	8.8	40	20.3	17.2	37.5	10.2	17
35.1	6.8	41.9	6.4	37	20.0	19.1	39.1	8.6	30
30.3	12.4	42.7	5.6	75	20.0	19.8	39.8	7.9	42
35.0	7.9	42.9	5.4	78	20.0	21.8	41.8	5.9	77
30.3	14.7	45.0	3.3	138	20.0	24.2	44.2	3.5	145
30.3	17.0	47.3	1.0	257	20.0	26.9	46.9	0.8	270
30.3	17.6	47.9	0.4	378	20.3	27.0	47.3	0.4	387
30.2	18.0	48.2	0.1	500	20.2	27.5	47.7	—	—
30.4	17.9	48.3	—	—					

The results show that mixtures of phosphorus vapour and oxygen at pressures below the explosion limit become, on exposure to light from a zinc spark or mercury arc, more susceptible to explosion, thereby resulting in a displacement of the lower explosion limit towards smaller pressures (Table V, col. 4). This effect, however, is not permanent, but decays slowly with time, the original explosion pressure being very nearly reached when the illuminated mixture has stood for 5—6 minutes after cessation of illumination. The rate of decay and amount of displacement of the lower limit evidently depended



to some extent on the condition of the walls, for the rate of decay in a clean vessel differed considerably from that in one which had been in use a considerable time (Table IV). Although the rate of decay and amount of lowering are independent of the pressures of oxygen, yet the latter differed considerably from that obtained when no oxygen at all was present in the reaction vessel and only phosphorus vapour was exposed to illumination (Fig. 4).

FIG. 4



There are two possible explanations of the lowering of the explosion limit by the ultra-violet light. Illumination of the phosphorus-oxygen mixtures may result in the formation in the gas phase of some active substance with an appreciable time of survival: this could only cause the lowering of the lower explosion limit by increasing the rate of production of the chains. It was seen previously that the rate of decay depended to some extent on the condition of the walls, so it seems likely that the deactivation of the active substance would occur on the walls. From the decay curve it is obvious that, before being deactivated, an active molecule would make a very great number of collisions with the walls (of the order of  $10^4$ ), so such a molecule, if produced, would be active in virtue of its chemical properties rather than its high energy content.

On the other hand, owing to the low rate of decay, it is more likely that the displacement of the lower limit is due rather to a change in the surface of the walls than to the production of active centres in the gas phase. Now the propagating collisions in the phosphorus-oxygen, as in the phosphine-oxygen, reaction are almost 100% efficient, so in equation (7), which gives the condition for explosion,  $k_2 = k_3$ ; and since  $k_2$  is large,  $K^2/k_2$  is probably very small and therefore may be neglected. Introducing these simplifications into (7), we have

$$(\alpha - 1)k_3[P_4][O_2] = K([P_4] + [O_2]) \quad (9)$$

so that

$$[P_4][O_2] = K' \times \text{constant} \quad (10)$$

where  $K'$  expresses the efficiency of the deactivating collisions of  $X_O$  with the walls;  $K'$  will depend therefore on the surface of the walls, so that an alteration in this surface on illumination may result in an alteration in  $K'$  and so give rise to a displacement of the

explosion limit. Hence, it was necessary to examine the lowering effect with a view to decide whether this displacement was due to a variation in the condition of the walls, thereby increasing their power of reflecting the chains, or to the production of active molecules in the gas phase itself.

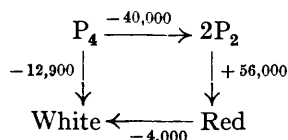
The principle of the method employed consisted in illuminating a mixture of phosphorus vapour and oxygen in one vessel A, and then immediately transferring it to a second vessel B, similar in all respects to that in which explosion pressure is measured. If the effect is a surface effect, the explosion pressure in B should be the same as that for a similar non-illuminated mixture, since the active surface is left behind. If, on the other hand, the active substance is present in the gas phase, it should produce in B a diminished explosion pressure. Before the experiments were started, phosphorus vapour and oxygen were allowed to combine explosively in both vessels, A and B, so that the conditions of the walls would be the same for both. The normal lowering effect was measured in A, both with and without illumination. Then A was filled with phosphorus vapour, which was illuminated for a definite time and transferred rapidly to B, where the pressure (time of flow) of the oxygen needed for the explosion was measured. The results (in the light of the mercury arc) were:

Explosion time in A = 54.2 secs.		
No illumination in A.	Illumination in A.	
Explosion in B.	Explosion in B.	Explosion in A.
56.9	57.1	51.0
57.5	57.0	53.0
56.8	56.6	51.2
57.0	56.9	50.7

It is seen that, although illumination of a phosphorus-oxygen mixture in A results in a displacement of the explosion pressure, yet if a similar illuminated mixture is transferred from A to B the explosion pressure obtained in B is the same as that for a non-illuminated mixture. There is no doubt, therefore, that the displacement of the lower explosion limit is due to alteration in the conditions of the surface of the reaction vessel, and not to a gas-phase effect (although the alteration in the surface may be the result of a change in the gas).

The results of the transfer experiments, together with the long rate of decay of the lowering effect found in previous experiments, show quite definitely that illumination of the phosphorus-oxygen mixtures below the lower limit results in a change in the surface conditions of the reaction vessel; and this alteration gives rise to a displacement of the lower explosion limit, which may be due either to an increase in the rate of initiation of the chains or to a decrease in efficiency of the deactivating collisions of the chain carriers with the walls. As the absorption of light by oxygen does not begin to be effective until much farther in the ultra-violet, the original cause of the lowering effect must lie in the absorption of the light by the phosphorus molecules.

During all these experiments a deposit of red phosphorus was formed on the walls after long illumination. In connexion with this, Melville and Gray (*Trans. Faraday Soc.*, 1936, **32**, 271) have shown that the mechanism for the production of red from white phosphorus *via* the gas phase is given by



the recombination of the  $P_2$  molecules to give red phosphorus occurring at a surface. Hence, since red phosphorus was deposited as a result of the absorption of light by phosphorus molecules, it follows that dissociation of these into  $P_2$  molecules (which recombine on the walls to give red phosphorus) must have occurred. This production of  $P_2$  molecules will also apply to the layer of phosphorus which was repeatedly shown to be adsorbed on the walls of the reaction vessel. Moreover, Gray found, when investigating the effect

of a heated filament on the transformation of white into red phosphorus, that the latter was deposited, not only on the walls of the reaction vessel, opposite the filament, but also in parts of the apparatus far removed from the source of the dissociation. It was obvious, therefore, since  $P_2$  molecules were reflected by the walls, that they had a considerable time of survival. (This observation was confirmed in later experiments.) Consequently, it seems very probable that, as a result of illumination, the surface of the reaction vessel becomes more or less covered with a layer of  $P_2$  molecules produced by the dissociation of  $P_4$  molecules in the gas phase and in the adsorbed surface layer. Although production of  $P_2$  molecules will stop on cessation of illumination, yet owing to their partial reflection by the walls, they can exist for a considerable time after this. Hence, it might be expected that the surface layer of  $P_2$  molecules and any phenomenon depending on their existence should persist for some time after illumination had ceased. Investigations of the effect of surface conditions on the lower explosion limits in many chain reactions have shown that in all cases the lower limit is extremely sensitive to changes in the condition of the walls (Thompson, *Z. physikal. Chem.*, 1930, B, 10, 273; Haber and Alyea, *Naturwiss.*, 1930, 18, 441; Sagulin, *Z. physikal. Chem.*, 1928, B, 1, 275). In this connexion, it is noteworthy that, after the reaction vessel had been cleaned and dried, a considerable number of explosions had to occur in the vessel before a constant value for the explosion pressure was reached. A similar phenomenon was observed by Garner and Coslett (*Trans. Faraday Soc.*, 1930, 26, 190) in the oxidation of carbon monoxide. There is no reason, therefore, for supposing that the alteration of the surface of the walls, due initially to the production of  $P_2$  molecules, is not sufficient to cause an increase in their reflecting power. This, by increasing the length of the chains, would result in a lowering of the explosion pressure.

It has been shown (Fig. 4) that the displacement of the lower limit was much greater when mixtures of phosphorus vapour and oxygen were illuminated than when phosphorus vapour alone was used; but although the displacement was increased by the presence of oxygen, it was independent of the oxygen pressure. This immediately suggested that the phenomenon was a surface effect, and led to a possible explanation for it. Illumination of phosphorus-oxygen mixtures by ultra-violet light will produce, both in the gas phase and on the walls,  $P_2$  molecules, which can, and do to some extent, recombine on the walls with the liberation of energy, eventually giving rise to a visible film of red phosphorus. Under these conditions, therefore, it seems certain that in the presence of oxygen, illumination will lead to the production of molecules of some lower oxide of phosphorus at the walls. The presence of these active oxide molecules (Semenoff suggested that a similar oxide was one of the chain carriers in the explosion reaction) would be expected to decrease the efficiency of the walls in breaking the chains, and result in the displacement of the lower limit; moreover, their existence would depend chiefly on the production and existence of the  $P_2$  molecules; for, although an increase in the pressure of oxygen would be expected to increase the rate of production of the oxide molecules, yet it would also facilitate their removal by oxidation to some higher oxide which would probably occur in the gas phase. On cessation of illumination, the concentration of  $P_2$  molecules would gradually decrease, owing partly to their combination to form red phosphorus and partly to their oxidation. Consequently, the active molecules on the surface would eventually disappear, thus giving rise to the slow decay of the lowering effect found on cutting off the ultra-violet light.

This explanation is only advanced tentatively, as no quantitative treatment of the problem is possible. Furthermore, the experiments carried out have not yielded the evidence required for the confident rejection of the other possible explanation of the displacement of the lower limit, *viz.*, that it is due to an increase in the rate of initiation of the chains owing to the production of active centres in the gaseous system by the ultra-violet light. In view of the fact that illumination of phosphorus-oxygen mixtures under identical conditions with those used above results in a little oxidation of the phosphorus vapour, this explanation, although contradictory to the predictions of the theory of chain reaction, is quite feasible. In this case, dissociation of  $P_4$  into  $P_2$  molecules by the ultra-violet light would probably lead to the formation of molecules of some oxide of phosphorus

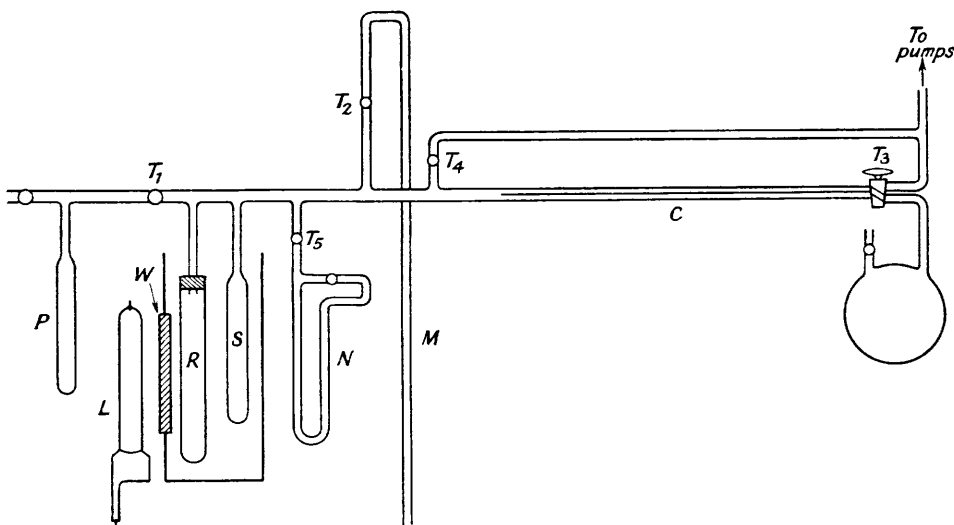
at the walls as before. These molecules would act as initiators by leaving the walls and starting chains in the gas phase. Thus illumination would lead to an increase in the rate of initiation of the chains which may be the cause of the displacement of the explosion limit. The number of initial centres, and hence the rate of initiation of the chains, would slowly decrease on shutting off the illumination, thus giving rise to a decay curve.

### PART III. THE INFLUENCE OF ULTRA-VIOLET LIGHT ON THE UPPER LIMIT.

Although the problem of the upper limit still awaits full elucidation, it is now generally accepted that deactivation of the chain carriers by the walls is negligible at this stage, rupture of the chains being due probably to collisions between the reactant molecules and the carriers in the gas phase. This theory was first suggested in connection with phosphine by Dalton (*Proc. Roy. Soc.*, 1930, *A*, **128**, 263). It is obvious, therefore, that the upper pressure limit of the phosphorus-oxygen reaction will depend on the balancing of two processes, *viz.*, the production of fresh active molecules by the branching of chains, and the deactivation process which takes place entirely in the gas phase. For the existence of an upper limit the second process must increase more rapidly than the first. It was shown in Part II that the lower explosion limit was lowered by the illumination. Although this effect was traced to the walls, no conclusive evidence was obtained as to whether this was due merely to an alteration of the rate of deactivation of the chain carriers owing to the altered surface conditions of the walls, or to an increase in active centres on the walls themselves. By working with mixtures of phosphorus vapour and oxygen at pressures above the upper explosion limit, conditions are obtained under which any alteration in the conditions of the surface of the reaction vessel would have no effect on this limit. Hence any displacement of the upper limit obtained by exposing such mixtures to light from a mercury arc must be due in some way to the production of active centres in the gaseous system, and not to an alteration in the rate of deactivation of the chain carriers at the surface.

The apparatus used for this part of the work (Fig. 5) was similar in form to that used in the experiments carried out at the lower limit. The silica reaction vessel was replaced by

FIG. 5.



a silica test-tube  $R$  ( $8'' \times \frac{3}{4}''$ ) cemented to the apparatus with "Picene" wax;  $S$  was a glass reservoir in which phosphorus vapour could be condensed by immersion in liquid air: it was shut off from the main phosphorus reservoir,  $P$ , by the tap  $T_1$ . As the pressures used were of the order of 200 mm. of mercury, it was necessary to keep the reaction vessel  $R$  and the

phosphorus reservoir *S* in a thermostat. This consisted of a metal box with a 6" × 1" silica window *W* fitted with a shutter, and at right angles to the silica window, a small glass window was fitted. With this arrangement it was possible to view *R* immediately after cessation of illumination. The temperature in the thermostat was kept sufficiently constant by passing a steady stream of water through it. No heating by the mercury arc was observed.

Pressures were measured by a capillary mercury manometer *M*, which was fitted with a wide bore tap *T*<sub>2</sub> so that it could be shut off from the reaction vessel when desired. The source of illumination was a mercury-vapour lamp, *L*, of the tungsten anode type, fitted with a water-cooled mercury cathode, and running on 4 amps. at 100 volts.

The method used was as follows. A little white phosphorus was condensed over from the main phosphorus reservoir into *S* by immersing the latter in liquid air, and oxygen was admitted up to a pressure greater than the upper explosion pressure. The liquid air was removed, and the reaction vessel and phosphorus reservoir immersed in the thermostat and left to attain the desired temperature. The total pressure was read on the manometer. By opening the two-way tap *T*<sub>3</sub> to the pumps, the pressure in *R* was slowly lowered until finally explosion took place, the pressure being read off the manometer.

After *R* and *S* had been pumped out, the reaction vessel was again filled with phosphorus and oxygen in the same way as before, but in this case the pressure of oxygen was kept just above the upper explosion limit. The mixture was then exposed to short illumination from the mercury lamp, and immediately after cessation of illumination, *R* was viewed to see if explosion had occurred, whilst *T*<sub>3</sub> was opened to the pumps. This procedure was the only one found suitable for testing the effect of ultra-violet light on the upper limit, for it was not possible to see any explosion occurring in *R* or to note the difference in pressure or in the rate of decrease in pressure during illumination, so that exposure to the mercury lamp could not be carried out whilst the excess oxygen was being pumped off. The pressure of phosphorus vapour in *R* was obtained from the temperature of the thermostat.

*Results.*—The results shown below are typical of those from a large number of experiments carried out in the above manner. Pressures of oxygen and phosphorus vapour are given in mm. of mercury.

Press. of P.	Initial press. of O <sub>2</sub> .	Press. of O <sub>2</sub> at which explosion occurred.	Illumination or not.	Press. of P.	Initial press. of O <sub>2</sub> .	Press. of O <sub>2</sub> at which explosion occurred.	Illumination or not.
0.012	521	478	No	0.009	528	389	No
0.012	520	520	Yes	0.009	526	526	Yes
0.012	552	552	Yes	0.009	530	389	No
0.012	579	495	No	0.009	516	516	Yes
0.012	579	579	Yes	0.009	526	495	No
0.012	550	550	Yes	0.009	542	542	Yes
0.012	581	550	No	0.009	584	584	Yes
0.012	621	468	No	0.009	580	404	No
0.012	629	629	Yes	0.009	626	352	Yes
				0.009	571	571	Yes
				0.009	579	400	No

It is seen that illumination of the reaction vessel causes a considerable displacement of the upper limit towards higher pressures—a phenomenon not predicted by theory. Furthermore, as deactivation of the chain carriers by collision with the walls of the reaction vessel is negligible, this displacement must be due to an increase in the number of active centres or initiators either in the gas phase itself or on the walls of the reaction vessel, due to absorption of the light by the phosphorus vapour. Since only the phosphorus vapour can appreciably absorb the wave-lengths of light used, these active centres must be P<sub>4</sub>, P<sub>2</sub>, or some phosphorus oxide molecules produced from these, and they will result in an increase in the rate of production of the chains, an effect which is counteracted by an increase in the rate of deactivation of the carriers by increasing the pressure so that explosion takes place at higher pressure than under normal conditions. This, however, is not in accordance with the predictions of the simple chain theory.

A possible explanation of the displacement lies in the tentative suggestion put forward by Melville and Roxburgh (*loc. cit.*) to explain a similar displacement of the upper limit in the phosphine-oxygen reaction, *viz.*, that, as the upper limit is very sensitive to the stationary concentration of one of the chain carriers X<sub>o</sub> (so that traces of water vapour and

changes in temperature exert a comparatively large effect on the upper limit), the limit obtained under normal conditions is not the true chain-theory explosion limit, but is much lower because the rate of starting of the chains is not sufficiently high for the relationship to hold. The displaced limit will therefore be nearer to the true explosion limit.

Owing to the difficulty experienced in obtaining a constant value for the upper explosion pressure, the above results could not be definitely confirmed, and consequently satisfactory experiments to determine (a) the duration of the displacement, (b) the effect on the displacement of altering the intensity of the light, could not be carried out.

#### PART IV. THE STABLE OXIDATION REACTION BELOW THE LOWER LIMIT.

From the preliminary investigations described in Part II, it was seen (Table II) that light from a zinc spark, besides displacing the lower critical oxidation limit in phosphorus-oxygen mixtures, also initiated a reaction between these elements at pressures where under ordinary conditions no reaction could be observed. Experiments (Melville, *Proc. Roy. Soc., A*, 1933, **139**, 555) have shown that a stable oxidation reaction, the kinetics of which display a very exact inter-relationship with the kinetics of the explosive reaction, can be initiated by a mercury arc (photosensitised reaction) or by a zinc spark (direct reaction) below the lower limit in the oxidation of phosphine. Obvious experimental difficulties (not encountered with phosphine) lay in the facts that (a) owing to the very low pressure of phosphorus vapour, the actual rate of reaction would be very small and therefore difficult to measure; and (b) there was shown to be a strongly adsorbed layer of phosphorus on the walls of the reaction vessel, so that direct measurements of the change in phosphorus pressure in this vessel were impossible. It was decided, however, to carry out an investigation of the oxidation reaction, and if possible to determine the kinetics of the reaction in order to find the probable relationship between the course of the reaction at and below the lower limit. Further, it was thought likely that additional information on the initiation of the chains might be obtained.

Before proceeding to a detailed investigation of the kinetics of the observed oxidation reaction, it was necessary to show that it possessed the characteristics of a chain reaction, and the most suitable of all the criteria by which this could be recognised in this case was the study of the effect on the rate of reaction of the addition to the system of small quantities of inert gases; for it would be expected that, if the reaction exhibits chain characteristics, the addition of small quantities of gases such as argon and nitrogen would result in an acceleration of the rate.

The apparatus shown in Fig. 5 was modified only in that *R* now consisted of a silica bulb fitted with a series of ground glass joints, so that it could be rotated on its axis and also easily removed for cleaning. The experimental procedure consisted in illuminating as before mixtures of phosphorus vapour and oxygen at the known pressures  $p_{F_2}$  and  $p_{O_2}'$  respectively, for requisite times, *T*. After illumination had ceased, the pressure of oxygen  $p_{O_2}''$  necessary to produce explosion in the mixture was measured, and the difference between the sum of the two pressures,  $p_{O_2}'$  and  $p_{O_2}''$ , and the normal explosion pressure,  $p_{O_2}$ , gave a measure of the rate of consumption of oxygen.

In the earlier investigation on the stable reaction below the lower limit, the above procedure was carried out with and without the presence of small quantities of argon and nitrogen, and the rates of oxidation in these cases compared. The pressure of inert gas was given by an oil manometer, *N*, which was shut off from the reaction vessel during experiments to prevent slight solution of the gases.

Now, it was shown in Part II that illumination of a phosphorus-oxygen mixture by the zinc spark displaced the lower limit towards lower pressures. This effect was not permanent, but disappeared on allowing the illuminated mixture to stand for 3—4 mins. after illumination had ceased. In the following experimental work, the reacting mixtures were allowed to stand for 4 mins. after cessation of illumination, so that by allowing this lowering effect time to decay, any error due to displacement of the critical pressure was avoided. This procedure was shown to have no effect on the explosion pressure under normal conditions. Trouble was experienced by the formation during illumination of a reddish-brown deposit on the walls of the reaction

vessel; since this was easily removed by heating (which caused inflammation) and also by treatment with bromine water, it was believed to be red phosphorus. It cut down the intensity of illumination considerably. By setting up a square sheet of metal with an aperture of 1.5 cm. radius immediately in front of the reaction vessel, and rotating the latter on its axis after each reading, about a dozen exposures could be made without having to remove the bulb for cleaning.

For most experiments a tungsten anode mercury lamp, with a water-cooled cathode, and fitted with a chromium-plated reflector, was found to be more suitable as a source of illumination than the zinc spark. As in Part II (see p. 1506), all traces of mercury vapour were excluded from the reaction vessel.

*Results.*—The results of a number of experiments carried out on the effect of inert gases on the rate of the oxidation reaction initiated by ultra-violet light below the lower limit are given in Table VI. During these experiments the intensity and length of illumination and pressures of oxygen and phosphorus vapour were kept constant whilst different pressures of argon and nitrogen ranging from 0.0 to 0.057 mm. were added. The pressure of inert gas is given in mm. of mercury, and that of oxygen is expressed by the time (in seconds) during which it entered the vessel;  $T$  denotes the period of illumination (in mins.).

TABLE VI.

Mercury arc. Pressure of phosphorus = 0.004 mm. Hg.  
From calibration curve: 1 sec. =  $6.91 \times 10^{-4}$  mm. Hg.

<i>Argon.</i>					<i>Nitrogen.</i>				
Initial concn. of O <sub>2</sub> (secs.).	Press. of A.	Time for explosion (secs.).	Amount of O <sub>2</sub> used (secs.).	$T$ (mins.).	Initial concn. of O <sub>2</sub> (secs.).	Press. of N <sub>2</sub> .	Time for explosion (secs.).	Amount of O <sub>2</sub> used (secs.).	$T$ (mins.).
0	—	71.1	—	—	0	—	70.8	—	—
0	0.028	54.4	—	—	0	0.013	61.7	—	—
36.3	—	39.8	5.0	3	36.5	—	39.3	5.0	3
36.3	0.028	26.3	8.2	3	36.5	0.013	31.0	5.8	3
0	—	71.0	—	—	0	—	70.2	—	—
0	0.057	43.8	—	—	0	0.026	55.1	—	—
36.5	—	39.7	5.2	3	36.5	—	38.4	4.7	3
36.4	0.057	18.1	10.7	3	36.5	0.026	25.4	6.8	3
0	—	70.5	—	—	0	—	71.3	—	—
0	0.027	55.2	—	—	0	0.039	50.0	—	—
36.3	—	39.6	5.4	3	36.6	—	39.8	5.1	3
36.3	0.027	26.0	7.1	3	36.6	0.039	20.5	7.1	3
0	—	71.0	—	—	0	—	70.2	—	—
0	0.057	43.7	—	—	0	0.052	46.4	—	—
36.4	—	39.6	5.0	3	36.5	—	38.8	5.1	3
36.4	0.057	18.3	11.0	3	36.5	0.052	19.8	9.9	3

The above tables show that the presence of an inert gas in a phosphorus-oxygen mixture results in an acceleration of the rate of oxidation below the lower limit, thus proving that this reaction, initiated by the ultra-violet light, is a chain reaction. Argon has a slightly greater accelerating effect than nitrogen, as is to be expected, since the smaller mass and diameter of the latter are not quite so effective in preventing the reaction chains from reaching the walls of the containing vessel.

Now, although the theory of the kinetics of the explosion limits in the phosphorus-oxygen reaction has been satisfactorily worked out, yet in order to apply it to the stable reaction, some modification had to be made. Consider the reaction taking place in the following stages:

(1) Some process by which the chain carrier  $X_p$  is formed. Let the rate of production be  $F(c)$ . Since there is no appreciable absorption of radiation from a zinc spark by oxygen, only  $X_p$  will be formed spontaneously.

- (2)  $O_2 + X_p \longrightarrow X_o$  . . . . . velocity coeff. =  $k_2$
- (3)  $X_o + P_4 \longrightarrow X_p$  . . . . . velocity coeff. =  $k_3$
- (4) Deactivation of  $X_o$  . . . . . velocity coeff. =  $K$
- (5) Deactivation of  $X_p$  . . . . . velocity coeff. =  $K$

( $X_o$  is the chain carrier derived from the oxygen molecule, possibly an oxygen atom, whilst  $X_p$  is the chain carrier resulting from the reaction between  $X_o$  and phosphorus.)

As the reaction takes place below the lower limit, deactivation of  $X_o$  and  $X_p$  occurs on the walls, and it is assumed that the rates at which  $X_o$  and  $X_p$  are destroyed in this manner are the same. If this was not the case, and one chain carrier was more easily destroyed than the other, it could easily be shown that the equation for the lower explosion limit would be  $[P_4]/([P_4] + [O_2]) = \text{const.}$  or  $[O_2]/([P_4] + [O_2]) = \text{const.}$ , which is not in such good agreement with experiment as the equation  $[P_4][O_2] = \text{constant.}$

Below the lower limit, the stationary concentrations of the carriers are given by

$$d[X_o]/dt = k_2[X_p][O_2] - k_3[X_o][P_4] - K[X_o] = 0 \quad \dots (11)$$

$$d[X_p]/dt = F(c) + k_3[X_o][P_4] - k_2[X_p][O_2] - K[X_p] = 0 \quad \dots (12)$$

Now

$$F(c) = K([X_p] + [X_o])$$

hence

$$[X_o] = F(c)/K - [X_p] \quad \dots (13)$$

and

$$[X_p] = \frac{k_3[P_4]F(c) + KF(c)}{k_2K[O_2] + k_3K[P_4] + K^2} \quad \dots (14)$$

If the chain length is great,  $KF(c)$  can be neglected in comparison with  $k_3[P_4]F(c)$ ;  $K^2$  can be neglected also, because  $k_3[P_4]$  and  $k_2[O_2]$  are large in comparison with  $K$ ;  $k_2$  can be taken as equal to  $k_3$ , since the propagating collisions are assumed to be almost 100% efficient.

Then

$$[X_p] = [P_4]F(c)/K([O_2] + [P_4]) \quad \dots (15a)$$

Now let  $K' = K[O_2] + [P_4] + [A]$ , *i.e.*,  $K'$  expresses the efficiency of deactivating collision with the walls,  $[A]$  being the concentration of inert gas. Therefore

$$[X_p] = [P_4]F(c)/K' \text{ if } [A] = 0 \quad \dots (15b)$$

and

$$-d[O_2]/dt = k_2[O_2][X_p] = k_2[O_2][P_4]F(c)/K' \quad \dots (16)$$

If  $I$  is the intensity of the incident light, then for the direct reaction,  $F(c) \propto I[P_4]$ , since the amount of absorption is very small. Hence

$$-d[O_2]/dt \propto k_2[O_2][P_4]^2I/K' \quad \dots (17)$$

*Results.*—Table VII shows a series of results obtained from experiments in which the intensity of the light and the pressure of phosphorus vapour were kept constant whilst the pressure of oxygen was varied;  $T$ , here and subsequently, is the period of illumination. The pressures of oxygen are expressed in seconds (1 sec. =  $6.907 \times 10^{-4}$  mm. Hg.). The constancy of the values of  $R/[O_2]^2$  shows that the rate of reaction is proportional to the square of the oxygen pressure.

TABLE VII.

Press. of phosphorus (mm. Hg)	0.004	0.004	0.004	0.004	0.004
Press. of $O_2$ (secs.)	30.0	20.0	10.0	37.0	30.0
$T$ (mins.)	$\Delta p$ (secs.)	$\Delta p$ (secs.)	$\Delta p$ (secs.)	$\Delta p$ (secs.)	$\Delta p$ (secs.)
0.5	4.0	2.0	0.5	6.2	3.7
1.0	7.6	3.5	1.4	9.8	7.8
2.0	12.2	6.2	2.9	15.0	12.0
3.0	15.1	8.5	4.2	18.9	15.5
4.0	17.2	11.0	4.0	20.5	17.1
5.0	19.0	11.8	5.0	21.9	18.6
Initial rate, $R$	10.0	4.12	1.57	18.0	10.3
$R/[O_2]^2$	0.011	0.010	0.016	0.013	0.012

Another series of experiments (with the mercury-vapour lamp) is given in Table VIII, in which the intensity of the light and oxygen pressure (expressed in the same units as in Table VII) were kept constant while the pressure of phosphorus vapour was varied. From the values obtained for  $R/[P_4]$  and  $t[P_4]$ , where  $t$  is time taken for a pressure change of  $5.27 \times 10^{-3}$  mm. to occur, it is seen that the rate of reaction,  $-d[O_2]/dt$ , is directly proportional to the pressure of phosphorus vapour.



TABLE VIII.

Press. of O <sub>2</sub> (secs.) .....	30.0	30.0	30.0	30.0	30.0	30.0
Press. of phosphorus .....	0.004	0.009	0.007	0.009	0.013	0.004
<i>T</i> (mins.).	$\Delta p$ (secs.).	$\Delta p$ (secs.).	$\Delta p$ (secs.).	$\Delta p$ (secs.).	$\Delta p$ (secs.).	$\Delta p$ (secs.).
1	0.9	2.0	1.3	2.0	2.5	1.0
3	2.5	5.0	3.6	5.9	7.2	2.4
3	2.4	5.2	3.9	5.2	6.8	2.4
6	4.4	10.2	6.9	10.5	11.8	4.3
6	4.8	10.2	8.3	10.1	11.9	4.3
10	6.8	15.0	12.0	14.9	17.3	6.8
10	7.3	11.7	11.9	15.1	16.5	7.5
Initial rate, $R \times 10^3$ .....	0.55	1.22	0.88	1.32	1.72	0.60
$R/[P_4]$ .....	0.14	0.14	0.13	0.15	0.13	0.15
<i>t</i> , secs. ....	11.6	4.8	6.3	4.5	3.6	12
$t \times [P_4]$ .....	0.046	0.043	0.044	0.040	0.047	0.048

Inspection of equation (17) shows that the rate of reaction should be directly proportional to the light intensity, *I*. Table IX shows results obtained from a series of experiments in which the pressures of phosphorus vapour and oxygen were kept constant while *I* was varied by use of a carbon tetrachloride-cyclohexane intensity filter. (Care was taken that the exposure was not so long as to cause decomposition of the filter.) The constancy of the values obtained for  $R/I$  shows that the rate is proportional to the first power of the intensity.

TABLE IX.

	Mercury arc.				Press. of phosphorus vapour, 0.007 mm.				Press. of O <sub>2</sub> , 55.0 secs.				
<i>I</i> .....	1.0	0.71	0.46	0.26	1.00	0.71	0.46	0.26	1.00	0.71	0.46	0.26	1.00
<i>R</i> .....	8.0	5.7	3.5	1.9	7.7	5.9	4.1	2.0	7.7	6.0	3.8	2.1	7.9
$R/I$ .....	8.0	8.0	7.7	7.3	7.7	8.3	8.9	7.7	7.7	8.4	8.3	8.0	7.9

From the results shown in Tables VII, VIII, and IX, it is seen that the kinetics of the stable oxidation reaction can be expressed by

$$-d[O_2]/dt = R = [O_2]^2[P_4] \times I \times \text{constant} \quad . \quad . \quad . \quad (18)$$

The chain theory, however, as shown in equation (17), indicates that the rate of reaction  $-d[O_2]/dt$  should be directly proportional to the square of the pressure of phosphorus vapour and to the first power of the oxygen pressure. This difference can be explained on the following lines, and is suggestive of a possible mechanism for the initiation of the chains. Although Semenoff's theory indicates that the length of chains in the phosphorus-oxygen reaction is proportional to the concentration of phosphorus molecules, he himself found experimentally that it was proportional to the square root of this concentration, and this relationship has been confirmed by Melville in his tungsten-filament experiments, and by other work on the same reaction. It was suggested, also, that the rate of starting of the chains was not proportional to the phosphorus concentration but to its square root. Hence, if chain length and the rate of initiation of the chains in the photochemical reaction are each proportional to  $[P_4]^{\frac{1}{2}}$ , then the rate of reaction will be proportional to first power only, and not to the square of the concentration of phosphorus molecules.

The deposition of red phosphorus on the walls of the reaction vessel during those and other experiments suggests that the initial effect of illumination of phosphorus-oxygen mixtures by ultra-violet light is the production of P<sub>2</sub> molecules owing to the dissociation of the P<sub>4</sub> molecules in the mixture. Moreover, illumination of such mixtures in this manner results in a change in the condition of the surface of the walls of the containing vessel, so it appears extremely likely (although it cannot be proved) that initiation occurs on the walls. Gray has shown that initiation of chains in phosphorus-oxygen mixtures below the lower limit, by a heated tungsten filament, is due to the combination of oxygen molecules with the adsorbed layer of phosphorus on the filament. This resulted in an escape from the gas surface of some lower oxide of phosphorus which is capable of initiating chains in the gas phase. Semenoff had previously suggested, however, that the pro-

duction of initiators in the explosive reaction was due to a very slow heterogeneous oxidation of phosphorus occurring at the walls of the reaction vessel. Consequently, it is not illogical to suppose that the initiation of chains in the photochemical reaction is due to the production of  $P_2$  molecules, which form at the surface of the walls of the reaction vessel some lower oxide of phosphorus, and it is this oxide that actually initiates the chains in the gas mixture. As the rate of initiation in this case would depend on the equilibrium  $[P_2]^2 = k_1[P_4]$ , this would account for the rate of initiation being proportional to the square root of the concentration of phosphorus molecules.

Doubt may reasonably exist, however, as to whether the equilibrium  $P_4 \rightleftharpoons 2P_2$  is really established in the presence of oxygen. It might be considered probable that the reaction between  $P_2$  and oxygen would be so rapid that the  $P_2$  molecules never reached the equilibrium concentration, and that the rate of reaction would then be proportional to  $[P_4]^{1.5}$ . The range over which the pressure of phosphorus vapour has been varied is not so wide as to exclude this possibility altogether. On the other hand, experiments on the production of red phosphorus indicate a considerable life time for the  $P_2$  molecules, and as red phosphorus is actually formed in sufficient quantities to be a nuisance, this implies a considerable concentration of  $P_2$  molecules.

In addition to this, if the production of one of the chain carriers  $X_p$  is due to the formation on the walls of a lower oxide of phosphorus, and not merely to the dissociation or activation of the phosphorus molecules by the ultra-violet light, then the rate of reaction would be proportional to the square of the concentration of oxygen molecules, and not to the first power as indicated by theory. In the production of the chain carrier  $X_p$  due to absorption of light of intensity  $I$ , the rate will be given by  $F(c) = I[O_2][P_4]^{\frac{1}{2}} \times \text{const.}$  and not by  $F(c) = I[P_4] \times \text{const.}$  as indicated by theory. Hence, as the rate of reaction is given by  $-d[O_2]/dt = k_2[O_2][P_4]^{\frac{1}{2}}F(c)/K'$  then

$$-d[O_2]/dt = [O_2]^2[P_4]I \times \text{constant} \quad \dots \quad (19)$$

so that the rate of reaction will be proportional to the square of the concentration of oxygen, as was found by experiment.

*Effect of Inert Gases on the Reaction.*—Preliminary experiments (Table VI) have shown that the presence of an inert gas results in an acceleration of the stable oxidation reaction. The following quantitative treatment of the effect of inert gases on the stable reaction is based on Semenov's expression for the length of reaction chains in the phosphorus-oxygen reaction. In view of the results of previous experimental work, it will now be assumed that the reaction is propagated through the gas phase, the chains being initiated on the surface of the walls. Then the length of the chains is given by

$$p_{P_2} p_{O_2} d^2 [1 + p_X / (p_{P_2} + p_{O_2})]$$

If  $f(p_{O_2}, p_{P_2})$  represents the rate of starting of the chains, then the rate of reaction  $-d[O_2]/dt$  will be expressed by

$$-dp_{O_2}/dt = K' f(p_{P_2}, p_{O_2}) p_{P_2} p_{O_2} [1 + p_X / (p_{P_2} + p_{O_2})] d^2 \quad \dots \quad (20)$$

where  $K'$  is a constant. But it has been shown [see (19)] that, if the intensity of the light is kept constant, the rate of reaction is given by

$$-dp_{O_2}/dt = p_{O_2}^2 p_{P_2} \times \text{constant} \quad \dots \quad (21)$$

so that the value of  $f(p_{O_2}, p_{P_2})$  must be independent of the concentration of phosphorus vapour. The rate of reaction will now be given by

$$-dp_{O_2}/dt = K'' p_{O_2}^2 p_{P_2} [1 + p_X / (p_{P_2} + p_{O_2})] d^2 \quad \dots \quad (22)$$

But if  $p_{P_2}$  and  $d$  are maintained at constant values, this can be simplified to

$$-dp_{O_2}/dt = K p_{O_2}^2 [1 + p_X / (p_{P_2} + p_{O_2})] d^2$$

Rearranging and integrating, we have

$$-Kt = \int \frac{dp_{O_2}}{p_{O_2}^2 [1 + p_X / (p_{P_2} + p_{O_2})]} \quad \dots \quad (23)$$

Finally we obtain

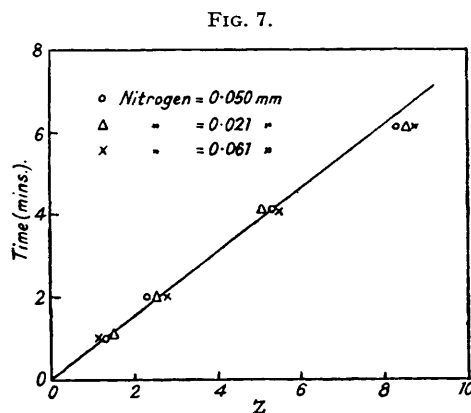
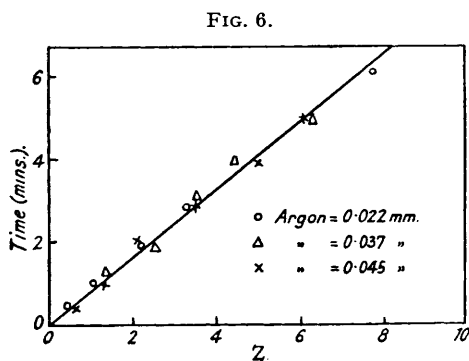
$$-Kt = \frac{1}{p_{P_4} + p_X} \left( -\frac{p_{P_4}}{p_{O_2}} + \frac{p_X}{p_{P_4} + p_X} \cdot \log \frac{p_{O_2}}{p_{O_2} + p_{P_4} + p_X} \right) + \text{const.} \quad (24)$$

There is a further complication to be disposed of in that  $p_X$  must be multiplied by the appropriate inert-gas factor  $\mu$ , in order to correct for the variation of the diffusion coefficient of the chain propagators in the different inert gases. Introducing this correction and evaluating the constant of integration, we have for the velocity constant  $K$

$$Kt = Z = \frac{1}{p_{P_4} + \mu p_X} \left[ \frac{p_{P_4}}{p_{O_2}} - \frac{p_{P_4}}{p_{O_2}'} + \log \left( \frac{p_{O_2}'}{p_{O_2}} \cdot \frac{p_{O_2} + p_{P_4} + \mu p_X}{p_{O_2}' + p_{P_4} + \mu p_X} \right)^{\mu p_X / (p_{P_4} + \mu p_X)} \right] \quad (25)$$

where  $p_{O_2}$  and  $p_{O_2}'$  are the initial and the final pressure of oxygen for a given reaction time  $t$ .

A series of experiments was carried out with different pressures of inert gases and various times of illumination. The inert gases were argon and nitrogen. Typical sets of results



obtained from these experiments are shown in Table X and also graphically in Figs. 6 and 7, where  $Z$  is plotted against  $t$ . It is seen from this that the velocity constant calculated from the above is independent of the concentration of inert gases.

TABLE X.

Argon.

Press. of A (mm.).	Initial concn. of O <sub>2</sub> (secs.).	Amount of O <sub>2</sub> used (secs.).	Initial concn. of O <sub>2</sub> . Final concn. of O <sub>2</sub> .	Z.	T (mins.).
0.032	40.2	14.0	1.53	7.66	6.0
0.032	40.2	11.1	1.38	5.52	4.0
0.032	40.1	5.4	1.16	2.36	2.0
0.032	40.0	3.2	1.09	0.92	1.0
0.032	40.1	1.2	1.04	0.58	0.5
0.045	40.1	19.8	1.98	11.9	6.0
0.045	40.0	13.4	1.50	6.12	5.0
0.045	40.2	17.2	1.75	8.70	6.0
0.045	40.2	11.6	1.41	4.93	4.0
0.045	40.0	18.6	1.27	3.43	3.0
0.045	40.3	9.0	1.29	3.57	3.0
0.045	40.1	5.5	1.16	2.02	2.0
0.045	39.9	7.5	1.37	3.08	2.0
0.045	40.1	3.0	1.09	0.74	0.5
0.045	40.2	3.6	1.10	1.30	1.0
0.037	40.3	13.8	1.52	6.96	5.0
0.037	40.3	9.6	1.31	4.29	4.0
0.037	40.2	7.9	1.25	3.43	3.0
0.037	40.3	6.4	1.19	2.71	2.0
0.037	40.2	3.3	1.09	1.28	1.0

## Nitrogen.

Press. of N <sub>2</sub> (mm.).	Initial concn. of O <sub>2</sub> (secs.).	Amount of O <sub>2</sub> used (secs.).	Initial concn. of O <sub>2</sub> Final concn. of O <sub>2</sub>	Z.	T (mins.).
0.050	35.2	13.2	1.60	8.64	6.0
0.050	35.2	9.2	1.35	5.23	4.0
0.050	35.2	6.6	1.23	2.39	2.0
0.050	35.4	2.8	1.09	1.28	1.0
0.021	35.2	10.2	1.41	8.96	6.0
0.021	35.2	6.3	1.22	4.82	4.0
0.021	35.2	3.5	1.11	2.48	2.0
0.021	35.2	1.9	1.06	1.27	1.0
0.061	35.0	15.0	1.75	9.44	6.0
0.061	35.1	10.4	1.42	5.47	4.0
0.061	35.2	6.4	1.22	2.95	2.0
0.061	35.2	2.8	1.09	1.17	1.0

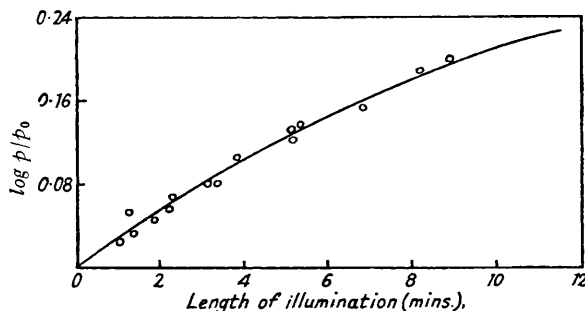
PART V. THE TRANSFORMATION OF WHITE INTO RED PHOSPHORUS  
BY MEANS OF ULTRA-VIOLET LIGHT.

In Parts II and IV, it was noted that ultra-violet light, besides catalysing the oxidation of phosphorus by oxygen, was apparently able to transform white into red phosphorus. When phosphorus vapour and oxygen were allowed to combine at slightly higher pressures than those used for the study of the stable reaction, however, no red phosphorus could be observed on the walls of the reaction vessel. Now, since it has been shown by various authors that the conversion of white into red phosphorus takes place through an intermediate stage, *i.e.*, through the formation of P<sub>2</sub> molecules, it was suggested that the initiation of the chains by ultra-violet light depends primarily on this dissociation of P<sub>4</sub> into P<sub>2</sub> molecules. It has not, however, been definitely shown that the absorption of light by P<sub>4</sub> molecules results in the formation of red phosphorus. Although it seems unlikely, it is possible that the production of red phosphorus may have been a result of the initiation of the chains, and not a result of a preliminary stage in the formation of the initiators of the chains.

At room temperatures, red phosphorus has practically no vapour pressure, so that the transformation of white into red phosphorus, if occurring at all, would seem to be a comparatively simple reaction. The velocity of this reaction could be followed by observing the change in pressure with time. Moreover,  $V$ , the chain length for any given pressure of oxygen and phosphorus vapour, is given by the ratio of the rate of oxidation to the rate of dissociation or clean-up of the phosphorus vapour, provided of course that the quantum yield be unity. In the following experiments, an attempt was made to observe and measure the transformation, and to obtain the value of the above ratio.

The method and apparatus were similar to those used in previous experiments, except that pressures and pressure changes were measured by means of a Pirani gauge.

FIG. 8.



*Results.*—A few typical runs (Table XI) showed that, as a result of illumination, red phosphorus was deposited fairly uniformly over the surface of the reaction vessel, the deposit being thickest, however, opposite the source of illumination. It is seen from Fig. 8 that this

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deposition occurs approximately according to a unimolecular equation. As the rate of reaction was very small, the Pirani gauge readings were not converted into pressures in terms of mm. of mercury, but are given in arbitrary units;  $t$  is the time (in minutes) required for  $\log p/p_0$  to reach the value 0.15, and  $T$  the time of illumination,  $p_0$  being the initial pressure and  $p$  that at a given time.

TABLE XI.

Pressure of phosphorus vapour = 0.015 mm. Hg.

Press. of phosphorus vapour, gauge units.	$\log p/p_0$ .	$T$ (mins.).	$t$ .	Press. of phosphorus vapour, gauge units.	$\log p/p_0$ .	$T$ (mins.).	$t$ .
1929	—	—	6.2	2506	—	—	6.9
1708	0.053	1.3		2311	0.035	1.4	
1523	0.103	4.0		2168	0.063	2.4	
1408	0.137	5.2		1960	0.107	5.9	
1213	0.202	9.1		1760	0.153	7.0	
1008	0.282	12.3		2052	—	—	
1634	—	—	6.7	1924	0.028	1.1	6.7
1498	0.037	1.9		1820	0.052	2.3	
1359	0.080	3.5		1707	0.080	3.3	
1068	0.185	8.4		1487	0.140	5.6	
727	0.352	19.3		1275	0.207	10.0	

Table XII gives results obtained from a series of experiments in which various pressures of an inert gas, argon, were added to a constant pressure of phosphorus vapour, and the rate of clean-up of the vapour measured, the intensity of illumination being kept constant and  $t$  in this case being the time required for  $\log p/p_0$  to reach the value 0.13.

TABLE XII.

Pressure of phosphorus vapour = 0.015 mm. Hg.

Press. of A (mm.).	$\log p/p_0$ .	$T$ (mins.).	$\frac{\log p/p_0}{T}$	$t$ (mins.).	Press. of A (mm.).	$\log p/p_0$ .	$T$ (mins.).	$\frac{\log p/p_0}{T}$	$t$ (mins.).
0.00	0.040	4.0	0.010	13.1	0.046	0.041	6.8	0.006	19.3
0.00	0.068	7.3	0.009		0.046	0.094	15.0	0.006	
0.00	0.091	10.0	0.009		0.070	0.041	9.4	0.004	
0.014	0.055	6.1	0.009	13.1	0.070	0.095	22.7	0.004	28.5
0.014	0.085	9.1	0.009		0.00	0.051	5.0	0.010	
0.031	0.037	3.6	0.010		0.00	0.073	8.1	0.009	
0.031	0.084	8.5	0.010	12.9	0.00	0.109	10.5	0.010	12.8
0.031	0.118	13.0	0.009						
0.031	0.146	16.6	0.008						

It is seen that addition of an inert gas at considerable pressure decreases the rate of transformation of white phosphorus into red. It may be concluded that illumination of  $P_4$  molecules by ultra-violet light causes their dissociation into  $P_2$  molecules, which can combine at the walls of the containing vessel to give red phosphorus. The presence of an inert gas would tend to prevent the drift of  $P_2$  molecules to the walls, and thus aid their recombination in the gas phase to give  $P_4$  molecules again. Hence the inert gas should, as was found for certain concentrations of the gas, decrease the rate of clean-up of the phosphorus vapour. However, when relatively very small concentrations of inert gas were added, no decrease in the rate of production of red phosphorus was observed. This suggests that only a fraction of the  $P_2$  molecules striking the walls form red phosphorus, the remainder being reflected from the surface; so, if the surface of the walls of the reaction vessel acts as a fairly efficient reflector of  $P_2$  molecules, no decrease in the rate of transformation of white into red phosphorus will be noticeable, until the rate of diffusion of the  $P_2$  molecules to the walls is seriously impeded. This is in keeping with the experimental results shown in Table XII. Furthermore, these results are in accordance with the suggestion that the formation of  $P_2$  molecules is one of the initial stages in the initiation of chains in phosphorus-oxygen mixtures at pressures below the lower critical oxidation pressure.

A few preliminary experiments were carried out in order to determine the rate of removal of phosphorus vapour in the presence of oxygen on illumination with ultra-violet light, so that by comparison with the rate of clean-up of phosphorus vapour under exactly similar con-

ditions, some idea of the lengths of the chains initiated in the stable oxidation could be obtained. The Pirani method was employed. Oxygen was allowed to enter the reaction vessel (containing phosphorus at a known pressure) through a previously calibrated capillary, until the required pressure was reached, and illumination was then commenced. After illumination had ceased, the phosphorus vapour was condensed out by means of liquid air, and the pressure of oxygen measured by taking the corresponding Pirani gauge reading. The oxygen was then pumped off, and the phosphorus warmed in a thermostat until the original pressure was reached, the Pirani reading again being taken. It was hoped thus to follow changes in pressure of both the oxygen and the phosphorus vapour, but although the former change could be measured, the latter could not, the pressure readings being very small and rather erratic. This probably was due to one or more of the following three possibilities. (i) That the change in phosphorus vapour was too small to be measured: this seems to be very unlikely in view of the measurements made in the clean-up. (ii) That a considerable quantity of phosphorus from the walls of the reaction vessel and side tubes would be condensed out, in addition to the phosphorus vapour, by the liquid air; it is possible, therefore, that on removal of the liquid air, the reaction vessel would only very slowly return to its original condition, so that pressure measurements would be useless. (iii) That the combination of phosphorus with oxygen did not result in its complete oxidation to phosphoric oxide; in that case some lower oxide with a measurable vapour pressure would be formed, so final measurements of the phosphorus pressure would include that of this lower oxide and would be inaccurate.

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