

KINETICS OF THE REACTION BETWEEN PHOSPHORUS VAPOUR
AND OXYGEN.

COMPARISON OF THE EFFECT OF HYDROGEN, DEUTERIUM AND
HELIUM ON THE LOWER EXPLOSION LIMIT OF PHOSPHORUS-
OXYGEN MIXTURES. DISPLACEMENT OF THE EXPLOSION LIMITS
BY THE ACTION OF ULTRAVIOLET LIGHT. STUDY OF THE
PHOTOCHEMICAL INITIATION OF THE STABLE REACTION BETWEEN
PHOSPHORUS VAPOUR AND OXYGEN.

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INTRODUCTION

PART I.

Comparison of the effect of Hydrogen, Deuterium, and Helium on the lower explosion limit of phosphorus-oxygen mixtures.

Chemical kinetics is that a chemical reaction can no longer be regarded as a series of independent elementary steps. This follows from the statement that in any system of elementary chemical reactions results in a definite change in the experimental condition of that system thus facilitating the onset of the next elementary reaction. Consequently the investigation of a chemical change may be suitably directed towards a study of the kinetics of the elementary steps which are set up and to the analysis of the elementary steps of energy transfer which determine their rates, aided by the study of the nature of the atoms and molecules which constitute the intermediate products of such a chemical change.

Careful investigation partly along these lines has led to the conclusion in the last few years that many of the reactions which are now being studied are of a type which are not yet understood.

I N T R O D U C T I O N

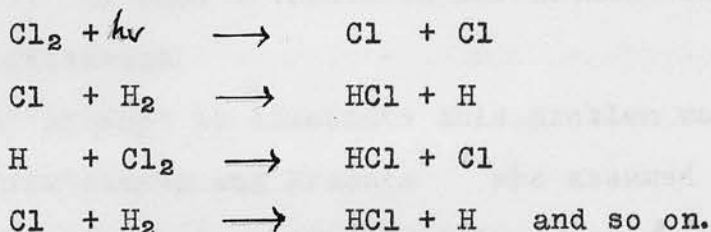
One of the most important theoretical conclusions resulting from the application of the chain theory to chemical kinetics is that a chemical reaction can no longer be regarded as a series of independent elementary stages. This follows from the statement that in any system an elementary chemical reaction results in a definite change in the statistical condition of that system thus facilitating the onset of the next elementary reaction. Consequently the investigation of a chemical change may be suitably directed towards a study of the kinetics of the stationary states which are set up and to the analysis of the elementary acts of energy transfer which determine these states, aided by the study of the nature of the atoms and unstable molecules constituting the intermediate products of such a chemical change.

Careful investigation partly along these lines has led to the conclusion in the last few years that many and indeed possibly most chemical reactions are chain

reactions. Seeing that the concept of a chain involves the idea of a series of reactions which may differ in order among themselves, the canonical classification of reactions into definite orders which followed the early development of the classical theory in chemical kinetics lost much of its significance with the introduction of the chain theory.

Although chain theories inevitably follow from the modern physical conception of the structure of molecules and the transfer of energy quanta on collision, the theory does present a logical development of the chemical concepts on chemical processes. The idea of a chain reaction developed from the work of Bodenstein in 1913 on the photosynthesis of HCl when he showed that the number of molecules of HCl formed was much greater than the number of light quanta absorbed. The enormous quantum yield of the order of 10^5 molecules of HCl per quantum of absorbed light energy was satisfactorily explained by Nernst¹ in terms of what is now known as the Nernst Chain. According to Nernst the initial stage in the reaction consisted in the production of atomic chlorine from the dissociation of the Chlorine molecule on the absorption of a quantum of light energy. Each atom of Chlorine thus formed can react with a molecule of Hydrogen with the formation of a HCl molecule and liberating a Hydrogen atom, which reacts with a Chlorine mol-

ecule again forming HCl but liberating an atom of Chlorine. Repetition of this process led to the development of the chains in the reaction mixture.



Thus as the chain was propagated by Hydrogen and Chlorine atoms, its development was only limited by the possibility of the recombination of the Hydrogen atoms or the Chlorine atoms on the walls of the containing vessel or in triple collisions with molecules of foreign gases when such are present, and by the adsorption of the Hydrogen and Chlorine atoms on the walls.

The idea of chains however was not applied to thermo-reactions until a much later date which is not surprising seeing that the only criterion of a chain reaction known at that period was the existence of an abnormally high quantum yield. The next advance in the subject was stimulated by the study of unimolecular reactions and in particular by the controversy over the origin of the energy of activation in such unimolecular reactions.² The difficulty arose over the fact that in a unimolecular reaction activation of molecules must come about, (except in definitely photochemical reactions), through the collision

of molecules so that the rate of activation should be proportional to the product of the concentrations, i. e. the reaction should be bimolecular, although this would be true only if the rate of reaction was determined by the rate of activation.

The first attempt to elucidate this problem was made in 1924 by Christiansen and Kramers^{3 4} who assumed that every product molecule in an exothermal reaction, carrying the original activation energy of the reactant together with the heat of reaction could energise other molecules on collision. This maintenance of a certain concentration of fresh activated molecules of reactant by the disappearance on collision of the activated product molecules enables the reaction to proceed according to the unimolecular law, in spite of the fact that activation is essentially a bimolecular process, the condition for this being that the pressure is sufficiently high to maintain the constant concentration of activated molecules.

The conception by Christiansen of chain mechanism played an important role in the elucidating of some remarkable phenomena of negative catalysis exhibited in a series of oxidation reactions. Shortly after Christiansen's publication Bäckstrom^{5 6} showed that the rate of oxidation of liquid aldehydes by gaseous oxygen was reduced considerably by the addition of small quantities

of certain substances. A similar phenomenon was observed in the oxidation of phosphorus dissolved in heptane and carbon tetrachloride.⁷ Christiansen's⁴ theory was able to give a satisfactory account of these phenomena by postulating that in both cases the reaction proceeds by a chain mechanism in which the chains were long. Consequently assuming that the inhibitors were capable of breaking the chains by uniting with one of the chain carriers then a very small quantity of the inhibitor would produce a considerable decrease in the rate of reaction. This supposition was fully supported by results obtained from experiments carried out on the corresponding photochemical reactions⁶ where large quantum yields were obtained. Moreover these quantum yields were found to diminish on addition of those substances acting as inhibitors to the thermal reaction.

In this way Christiansen established one criterion by which a chain mechanism in a thermal reaction could be recognised, viz. if in a homogeneous reaction the addition of small quantities of a foreign substance produces a marked inhibitive effect on the rate of reaction then the reaction must proceed by a chain mechanism.

In spite of the fact that the oxidation of Phosphorus and the phenomena accompanying it, had been studied for over a hundred years no satisfactory mechanism for the reaction was put forward until the development of the chain theory. Bäckstrom's⁷ experiments on the oxid-

ation of Phosphorus in heptane had led to the conclusion that the oxidation of Phosphorus was a chain reaction but no satisfactory mechanism for the initiation and development of chains was suggested. 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 Joubert⁸ about eighty years later. Between these two limits Phosphorus vapour and oxygen inflame. No satisfactory explanation of the existence of upper and lower limits was given by their discoverers.

Chariton and Walta⁹ showed that by the addition of argon to a P_4-O_2 mixture, inflammation could be provoked at lower pressures than in its absence. These experiments were repeated and confirmed by Semenov¹⁰ who in addition to this showed that the explosion pressure diminished on increasing the diameter of the containing vessel and that the lower limit could be defined by the equation: -

$$P_{P_4}^{k_2} \cdot P_{O_2} \left(1 + \frac{P_x}{P_{O_2} + P_{P_4}} \right) d^2 = \text{constant} \quad (1)$$

where d was the diameter of the vessel, and P_{P_4} , P_{O_2} , P_x , the pressures of phosphorus vapour and oxygen and of inert gas at the lower limit.

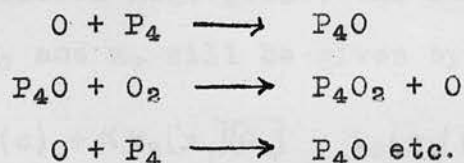
From these experiments Semenoff^{10 11 12} was able to develop in terms of the chain theory a quantitative treatment of the reaction. He suggested that the oxidation of phosphorus was a chain reaction in which the chain carriers were oxygen atoms and phosphorus oxide molecules, the chains being broken at the lower limit by adsorption of the chain 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 characterizing chain reactions Semenoff obtained an expression for the lower limit almost identical with that obtained from experimental results

$$p_{P_4} \cdot p_{O_2} \left(1 + \frac{p_x}{p_{P_4} + p_{O_2}} \right) d^2 = \text{Constant} \quad (2)$$

In deriving this expression Semenoff^{10 11 12} made several assumptions which when viewed in relation to the knowledge of the processes whereby excited atoms and molecules can lose their energy cannot be considered quite satisfactory. Moreover in obtaining the expression 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 com-

binning with oxygen molecules form P_4O_2 and regenerate free oxygen atoms again. Thus the following scheme represents according to Semenov the development of the primary reaction: -



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 the equation derived by Semenov is due to Dalton and Hinshelwood.¹³ In their method no assumption of a definite mechanism for the reaction is required. The chain propagators are designated x_o and x_p . x_o on collision with a phosphorus molecule gives rise to x_p whilst x_p on collision with an oxygen molecule produces x_o so that the chain develops until either x_o or x_p is destroyed at the walls. The procedure now is to obtain equations for the rate of production and removal of x_o and x_p and find where the 'stationary state' just ceases to be possible.

If $k_1F(c)$ is the original rate of production of x_o

in the reaction mixture, a function of the concentration of the reactants and $K[x_0]$ and $K[x_p]$ be the rates at which x_0 and x_p are deactivated at the walls, then at the lower limit seeing that deactivation in the gas phase is considered negligible, the stationary concentrations of x_0 and x_p will be given by

$$\frac{d[x_0]}{dt} = k_1 F(c) + \alpha k_2 [x_p][O_2] - k_3 [x_0][P_4] - K[x_0] = 0 \quad (3)$$

$$\frac{d[x_p]}{dt} = k_3 [x_0][P_4] - k_2 [x_p][O_2] - K[x_p] = 0 \quad (4)$$

α is a factor introduced to take into account the fact that branching of the chains does occur. It is assumed that the branching occurs only in the $x_p - O_2$ collisions so that α must be the mean number of x_0 molecules formed in an effective $x_p - O_2$ collision.

Solving (4) for x_p and substituting in (3) and solving for x_0 then,

$$[x_0] = \frac{k_1 k_2 [O_2] F(c) + k_1 K F(c)}{(1-\alpha) k_2 k_3 [P_4][O_2] + k_2 K [O_2] + k_3 K [P_4] + K^2} \quad (5)$$

Assuming perfect efficiency for the collisions between x & O_2 and between x_0 & P_4 then $k_2 = k_3$. Also K^2 may be neglected since K is probably very small in comparison with $k_2 [O_2]$ and $k_3 [P_4]$. The condition for explosion is that $[x_0]$ should increase indefinitely so the denominator of equation must be zero.

Introducing these simplifications into equation (5) and equating the denominator to zero we have,

$$(\alpha-1) k_3 [P_4] [O_2] = K \{ [O_2] + [P_4] \} \quad (6)$$

Since K determines the rate at which x_0 and x_p reach the walls then for a given vessel it is inversely proportional to the total pressure i.e.

$$K = \frac{K'}{[O_2] + [P_4] + [x]} \quad (7)$$

where $[x]$ is concentration of inert gas added.

Thus,

$$(\alpha-1) k_3 [P_4] [O_2] = \frac{K' \{ [P_4] + [O_2] \}}{[O_2] + [P_4] + [x]} \quad (8)$$

Now concentrations are proportional to partial pressures so that for a given tube

$$p_{P_4} \cdot p_{O_2} \left\{ 1 + \frac{p_x}{p_{P_4} + p_{O_2}} \right\} = \text{constant.} \quad (9)$$

Thus for a given pressure of phosphorus $1/p_{O_2}$ plotted against $1 + \frac{p_x}{p_{P_4} + p_{O_2}}$ should give a straight line.

Melville¹⁴ and Ludlam carried out a series of experiments at the lower limit using fourteen different inert gases and showed that Semenov's equation did hold provided that the concentration of the inert gas p_x was multiplied by some additional factor μ which depended on the nature of the inert gas present. It was found necessary, therefore to modify Semenov's equation to

$$p_{p_4} \cdot p_{o_2} \left(1 + \frac{\mu p_x}{p_{p_4} + p_{o_2}} \right) = \text{constant for a given tube.} \quad (10)$$

The factor μ was found to be inversely proportional to the diffusion coefficient of the chain carriers into the inert gas. Examination of the temperature coefficient of μ afforded additional evidence in support of the supposition that μ was dependent on the diffusion coefficient of the chain carriers into the inert gas.

The diffusion coefficient for a given mixture increases with temperature according to the law

$$f(T) = \frac{T^{\frac{3}{2}}}{1 + C/T} \quad (11)$$

where T is the absolute temperature and C is Sutherland's constant for the system in question. The product $f(T)$ into μ was found to be independent of the temperature.

Inquiry into the theoretical basis for the empirical change in Semenov's equation (2) was found to be 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. Semenov¹⁵ attempted a rigorous and exact solution of the problem for the hydrogen-oxygen reaction in which he assumed that the chain propagators were H atoms and HO₂ molecules. A more simple treatment of the problem can be obtained, after making certain assumptions which although not strictly correct are sufficiently justified for present

purposes, by proceeding along the following lines.

Consider a chain carrier diffusing through the ternary gas mixture for which the separate diffusion coefficients are D_1 , D_2 and D_3 . If t is the time taken for the carrier to diffuse a distance d , then t will be proportional to the sum of the reciprocals of the separate diffusion coefficients i.e.

$$t \sim \frac{1}{D_1} + \frac{1}{D_2} + \frac{1}{D_3} \quad (12)$$

According to the Stefan-Maxwell diffusion theory for binary mixtures D the diffusion coefficient is given by

$$D = \frac{K}{[A] + [B]} \cdot \frac{1}{G_{AB}^2} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{-\frac{1}{2}} \quad (13)$$

where G_{AB} is the sum of the molecular radii of A and B, M_A and M_B are the molecular weights of A and B respectively, and K is a constant. A in this case refers to the chain carriers which are probably a phosphorus oxide molecule and an oxygen atom or activated oxygen molecule. For the sake of simplicity the diameter and mass of the carriers are assumed to be the same. Now since the stationary concentration of the chain carriers as compared with the pressures of phosphorus, oxygen and inert gas will be extremely small, A may be neglected in the above equation.

Substituting for D in equation (12) then

$$t \sim \frac{[P_2]}{K} G_{A-B}^2 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}} + \frac{[O_2]}{K} G_{A-O_2}^2 \left(\frac{1}{M_A} + \frac{1}{M_{O_2}} \right)^{\frac{1}{2}} + \frac{[X]}{K} G_{A-X}^2 \left(\frac{1}{M_A} + \frac{1}{M_X} \right)^{\frac{1}{2}} \quad (14)$$

Now the inert gas factor $1 + \frac{\mu[X]}{[P_4] + [O_2]}$ must be the ratio of the time taken for the chain carriers to diffuse to the walls of the reaction vessel in the presence of an inert gas to the time taken in absence of such a gas. t_0 the time taken for a chain carrier to diffuse a definite distance in absence of an inert gas is given by

$$t_0 \sim \frac{[P_4]}{K} G_{A-P_4}^2 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{-\frac{1}{2}} + \frac{[O_2]}{K} G_{A-O_2}^2 \left(\frac{1}{M_A} + \frac{1}{M_{O_2}} \right)^{-\frac{1}{2}} \quad (15)$$

Hence

$$1 + \frac{\mu[X]}{[P_4] + [O_2]} = \frac{t_x}{t_0} = \frac{\frac{[P_4]}{K} G_{AB}^2 \left(\frac{1}{M_A} + \frac{1}{M_{P_4}} \right)^{-\frac{1}{2}} + \frac{[O_2]}{K} G_{A-O_2}^2 \left(\frac{1}{M_A} + \frac{1}{M_{O_2}} \right)^{-\frac{1}{2}} + \frac{[X]}{K} G_{AX}^2 \left(\frac{1}{M_A} + \frac{1}{M_X} \right)^{-\frac{1}{2}}}{\frac{[P_4]}{K} G_{A-P_4}^2 \left(\frac{1}{M_A} + \frac{1}{M_{P_4}} \right)^{-\frac{1}{2}} + \frac{[O_2]}{K} G_{A-O_2}^2 \left(\frac{1}{M_A} + \frac{1}{M_{O_2}} \right)^{-\frac{1}{2}}} \quad (16)$$

Now suppose

$$G_{A-P_4} = G_{A-O_2} = G_{AX} \text{ and } M_{P_4} = M_{O_2} = M_M$$

then equation (16) simplifies to

$$1 + \frac{\mu[X]}{[P_4] + [O_2]} = 1 + \frac{G_{AM}^2 \left(\frac{1}{M_A} + \frac{1}{M_X} \right)^{-\frac{1}{2}} \cdot \frac{[X]}{[P_4] + [O_2]}}{G_{AX}^2 \left(\frac{1}{M_A} + \frac{1}{M_M} \right)^{-\frac{1}{2}}} \quad (17)$$

i. e.

$$\mu = \frac{G_{AX}^2 \left(\frac{1}{M_A} + \frac{1}{M_M} \right)^{\frac{1}{2}}}{G_{AM}^2 \left(\frac{1}{M_A} + \frac{1}{M_X} \right)^{\frac{1}{2}}} \quad (18)$$

where G_{AM} and M_M are mean values - an approximation which is not serious for the P_4-O_2 reaction.

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 worthwhile investigating and comparing the inert gas effect obtained by using Hydrogen, Deuterium and Helium as inert gases, with a view to confirming the above expression, and also of completing the work on the effect of foreign gases on the lower critical oxidation limit previously carried out in this department.¹⁴

Now if M_A the mean molecular weight of the chain carriers is large in comparison with M_X , the molecular weight of the inert gas then $\frac{1}{M_A}$ may be neglected. The chain carriers in the P_4-O_2 reaction are assumed to be either an oxygen atom or 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, $\frac{1}{M_A}$ will be small and therefore neglected.

Also $\left(\frac{1}{M_A} + \frac{1}{M_M}\right)$ and G_{AM} remains constant for the P_4-O_2 reaction so that (18) becomes

$$\mu_X = \frac{k_1 G_{AX}^2}{k_2^2 \left(\frac{1}{M_X}\right)^{\frac{1}{2}}} \quad \text{where } k_1 = \left(\frac{1}{M_A} + \frac{1}{M_M}\right) \quad (19)$$

$$\text{and } k_2 = G_{AM}$$

Hydrogen and Deuterium have been shown to have the same molecular diameters^{16 17} 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 (19)

$$\frac{\mu_{He}}{\mu_{D_2}} = \frac{1}{\sqrt{2}}$$

Helium although possessing the same mass as Deuterium has been shown to have a slightly larger molecular diameter^{18 19} than Hydrogen and hence Deuterium, so that

$$\frac{\mu_{D_2}}{\mu_{He}} = \frac{G_{AD}^2}{G_{AHe}^2}$$

Any difference between the experimental values of μ_{D_2} and μ_{He} must be ascribed therefore to the difference in molecular diameter. Consequently it was interesting to see whether the small difference in molecular diameter was sufficient to cause any appreciable difference in the corresponding values of μ .

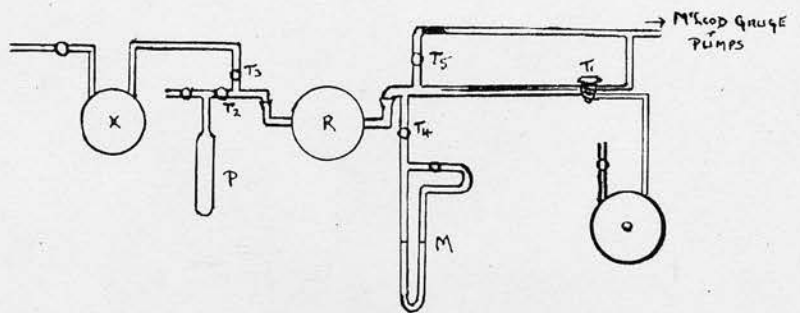


Fig I

EXPERIMENTAL

In determining the lower explosion pressure the inert gas and phosphorus vapour were introduced into the reaction vessel, and oxygen was allowed to slowly leak through a fine capillary into the reaction vessel. By determining previously, the rate of flow of oxygen the explosion pressure could be obtained from a measurement of the time elapsing between the starting of the oxygen flow and the occurrence of explosion.

The apparatus used is shown in Fig. I. The reaction vessel R was a silica bulb attached by means of ground glass joints to reservoirs of phosphorus and inert gases at one end and to a very fine capillary C at the other. The capillary was made by drawing down 1 mm. capillary until the diameter was less than 0.1 mm. - the length of capillary being about 20 cm. in length. It was protected by enclosing it in a glass tube.

Oxygen entered the reaction vessel R from O the oxygen reservoir by means of the two-way tap T, through the capillary C. By rotating the tap through 180° the

flow of oxygen could be instantly arrested. A mercury condensation pump backed by a Hyvac oil pump was used to effect exhaustion. The apparatus was fitted with a McLeod gauge for the purposes of calibration.

P the vessel containing white phosphorus could be immersed in a water-bath or in ice and water mixtures, whilst the inert gas reservoir X was fitted with a tap T_3 made in the form of a gas pipette for transferring small quantities of inert gas from X to R. The pressure in R due to the introduction of inert gas was measured by an oil manometer M also used to measure the rate of flow of oxygen through the capillary C. Apiezon oil B - vapour pressure 10^{-7} mms. Hg and thoroughly degassed before use, - was used in the manometer.

Movements of the oil surface in the oil manometer were observed by means of a microscope fitted with an eye piece scale. As the oxygen dissolved slightly in the oil, the manometer was shut off from the reaction vessel during experiments.

The rate of flow of oxygen into the reaction vessel was determined by opening the inlet tap T_1 and simultaneously starting a stop watch. After 60 seconds or so the inlet tap was rotated through 180° , the watch stopped and the increase in pressure showing on the manometer noted. Now as during experiments the manometer was shut off by tap T_4 from the reaction vessel, it was

necessary to determine the effect of closing the tap on the rate of flow of oxygen. Closing tap T_4 cut down the volume to $1/1.07$ of the original volume so that the rate of flow required to give the pressure of oxygen in R at any given time was 1.07 times the rate found above.

White phosphorus was prepared in the following manner: - Red phosphorus was suspended in a hot solution of sodium hydroxide until free from oxide, then washed, dried and sealed into the apparatus. It was heated gently at first in a good vacuum in order to expel all traces of water vapour and more strongly afterwards to convert it into white phosphorus. Finally the phosphorus was connected to the pumps for several hours and an appreciable quantity of white phosphorus removed thereby making certain that all traces of volatile oxides would be absent. The phosphorus pressure was regulated by immersing the reservoir in vacuum flasks containing water or salt solutions at the desired temperatures - the corresponding pressures being obtained from International Critical Tables.

Oxygen was obtained from cylinders and dried by passing it slowly through a liquid air trap. Hydrogen also from cylinders was freed from the oxygen it contained by passing it over palladised asbestos heated to 350°C , and dried by means of a liquid air trap. The following method was found to be the most suitable means

of preparing Deuterium. Sodium was distilled from a reservoir attached to an evacuated pyrex glass vessel until ^a metallic mirror formed on the walls of the vessel. Heavy water was contained in a side tube shut off from the main portion of the vessel by a pyrex tap. After removing the reservoir of sodium, the heavy water was brought into contact with the sodium mirror, thus forming Deuterium which was collected and stored in a glass reservoir. The sample of water used contained 99.95% D₂O.

Actual experiments were carried out in the following manner. R the reaction vessel was pumped out and filled with phosphorus vapour at a known pressure (obtained from the temperature of the bath in which the phosphorus reservoir was immersed). With taps T₂, T₃, T₄ and T₅ closed the flow of oxygen was started and the time elapsing before explosion occurred noted. The flow of oxygen was then stopped and R pumped out again. After admitting to R phosphorus vapour to the desired pressure the inert gas was introduced its pressure being recorded on the oil manometer. The gases were allowed a short interval for mixing - the oil manometer being shut off from R to avoid any possible slight solution of the gases in the oil - the flow of oxygen started and the explosion time obtained. From previous determinations of the rate of flow of oxygen through the capillary the amount of oxygen admitted to R could be

obtained. The rate of flow of oxygen was checked after every set of readings and the mean of two such results used in finding the absolute pressures of oxygen.

In carrying out experiments, operations such as pumping out the reaction vessel between explosions, and the time taken for filling the latter with phosphorus vapour and inert gas were standardised as far as possible.

Results.

Typical sets of results are given in the following tables, in which all pressures are in millimetres of mercury.

0.0131	0.0131	64.7	3.5
0.0131	0.0131	65.7	3.6
0.0131	0.0131	66.7	3.7
0.0131	0.0131	67.7	3.8
0.0131	0.0131	68.7	3.9
0.0131	0.0131	69.7	4.0
0.0131	0.0131	70.7	4.1
0.0131	0.0131	71.7	4.2
0.0131	0.0131	72.7	4.3
0.0131	0.0131	73.7	4.4
0.0131	0.0131	74.7	4.5
0.0131	0.0131	75.7	4.6
0.0131	0.0131	76.7	4.7
0.0131	0.0131	77.7	4.8
0.0131	0.0131	78.7	4.9
0.0131	0.0131	79.7	5.0
0.0131	0.0131	80.7	5.1
0.0131	0.0131	81.7	5.2
0.0131	0.0131	82.7	5.3
0.0131	0.0131	83.7	5.4
0.0131	0.0131	84.7	5.5
0.0131	0.0131	85.7	5.6
0.0131	0.0131	86.7	5.7
0.0131	0.0131	87.7	5.8
0.0131	0.0131	88.7	5.9
0.0131	0.0131	89.7	6.0
0.0131	0.0131	90.7	6.1
0.0131	0.0131	91.7	6.2
0.0131	0.0131	92.7	6.3
0.0131	0.0131	93.7	6.4
0.0131	0.0131	94.7	6.5
0.0131	0.0131	95.7	6.6
0.0131	0.0131	96.7	6.7
0.0131	0.0131	97.7	6.8
0.0131	0.0131	98.7	6.9
0.0131	0.0131	99.7	7.0
0.0131	0.0131	100.7	7.1
0.0131	0.0131	101.7	7.2
0.0131	0.0131	102.7	7.3
0.0131	0.0131	103.7	7.4
0.0131	0.0131	104.7	7.5
0.0131	0.0131	105.7	7.6
0.0131	0.0131	106.7	7.7
0.0131	0.0131	107.7	7.8
0.0131	0.0131	108.7	7.9
0.0131	0.0131	109.7	8.0
0.0131	0.0131	110.7	8.1
0.0131	0.0131	111.7	8.2
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0.0131	0.0131	160.7	13.1
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0.0131	0.0131	163.7	13.4
0.0131	0.0131	164.7	13.5
0.0131	0.0131	165.7	13.6
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0.0131	0.0131	169.7	14.0
0.0131	0.0131	170.7	14.1
0.0131	0.0131	171.7	14.2
0.0131	0.0131	172.7	14.3
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0.0131	0.0131	176.7	14.7
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0.0131	0.0131	178.7	14.9
0.0131	0.0131	179.7	15.0
0.0131	0.0131	180.7	15.1
0.0131	0.0131	181.7	15.2
0.0131	0.0131	182.7	15.3
0.0131	0.0131	183.7	15.4
0.0131	0.0131	184.7	15.5
0.0131	0.0131	185.7	15.6
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0.0131	0.0131	187.7	15.8
0.0131	0.0131	188.7	15.9
0.0131	0.0131	189.7	16.0
0.0131	0.0131	190.7	16.1
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0.0131	0.0131	211.7	18.2
0.0131	0.0131	212.7	18.3
0.0131	0.0131	213.7	18.4
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0.0131	0.0131	215.7	18.6
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0.0131	0.0131	220.7	19.1
0.0131	0.0131	221.7	19.2
0.0131	0.0131	222.7	19.3
0.0131	0.0131	223.7	19.4
0.0131	0.0131	224.7	19.5
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0.0131	0.0131	230.7	20.1
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0.0131	0.0131	237.7	20.8
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0.0131	0.0131	263.7	23.4
0.0131	0.0131	264.7	23.5
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0.0131	0.0131	293.7	26.4
0.0131	0.0131	294.7	26.5
0.0131	0.0131	295.7	26.6
0.0131	0.0131	296.7	26.7
0.0131	0.0131	297.7	26.8

Table No 1Hydrogen

Temperature of reaction vessel = 15°C.

Temperature of phosphorus reser. = 0°C.

P_x	P_{O_2}	$\frac{1}{P_{O_2}}$	$\frac{P_x}{P_{O_2} + P_{O_2}}$
0	0.0208	48.0	0
0.0232	0.0191	52.3	1.0
0.0232	0.0191	52.3	1.0
0.0480	0.0175	57.1	2.1
0.0460	0.0179	55.9	2.1
0.0680	0.0154	64.9	3.5
0.0680	0.0150	66.7	3.6
0.0692	0.0159	62.7	3.5
0.0914	0.0136	73.6	5.1
0.0910	0.0143	69.9	5.0
0.0120	0.0126	79.3	6.7
0.0120	0.0126	79.3	6.7
0.1342	0.0108	92.6	9.1
0.1342	0.0111	90.2	8.9
0.1574	0.0104	96.1	10.9
0.1568	0.0100	100	11.2
0.1811	0.0090	111	14.0
0.1820	0.0088	114	14.2
0	0.0208	48.0	0

Table No 2Deuterium

Temperature of reaction vessel = 15°C.

Temperature of phosphorus reservoir = 0°C.

P_x	P_{O_2}	$\frac{1}{P_{O_2}}$	$\frac{P_x}{P_{P_4} + P_{O_2}}$
0	0.0208	48.0	0
0.0198	0.0189	52.9	0.9
0.0198	0.0195	51.3	0.8
0.0390	0.0161	62.3	1.9
0.0390	0.0166	60.2	1.9
0.0591	0.0144	69.5	3.2
0.0596	0.0147	67.9	3.2
0.0764	0.0132	75.7	4.5
0.0782	0.0128	78.1	4.7
0.0986	0.0117	85.5	6.3
0.0986	0.0117	85.5	6.3
0.1119	0.0107	93.5	7.6
0.1108	0.0109	91.8	7.4
0.1275	0.0100	100	9.1
0.1275	0.0092	109	9.6
0.1376	0.0089	112	10.7
0.1380	0.0088	114	10.8
0.	0.0208	48.0	0

Table No 3Helium

Temperature of reaction vessel = 15°C.

Temperature of phosphorus reservoir = 0°C.

P_x	P_{O_2}	$\frac{l}{P_{O_2}}$	$\frac{P_x}{P_{P_4} + P_{O_2}}$
0	0.0208	48.0	0
0.0161	0.0190	53.0	0.8
0.0161	0.0196	51.0	0.7
0.0315	0.0178	56.2	1.4
0.0321	0.0172	58.1	1.5
0.0470	0.0156	64.1	2.4
0.0470	0.0156	64.1	2.4
0.0626	0.0141	70.8	3.4
0.0620	0.0139	72.1	3.6
0.0786	0.0132	75.8	4.6
0.0780	0.0129	77.5	4.6
0.0946	0.0118	84.7	6.0
0.0954	0.0122	82.0	5.9
0.1095	0.0106	94.3	7.5
0.1100	0.0106	94.3	7.3
0.1246	0.0092	109	9.4
0.1250	0.0095	105	9.2
0.1413	0.0084	119	11.4
0	0.0208	48.0	0

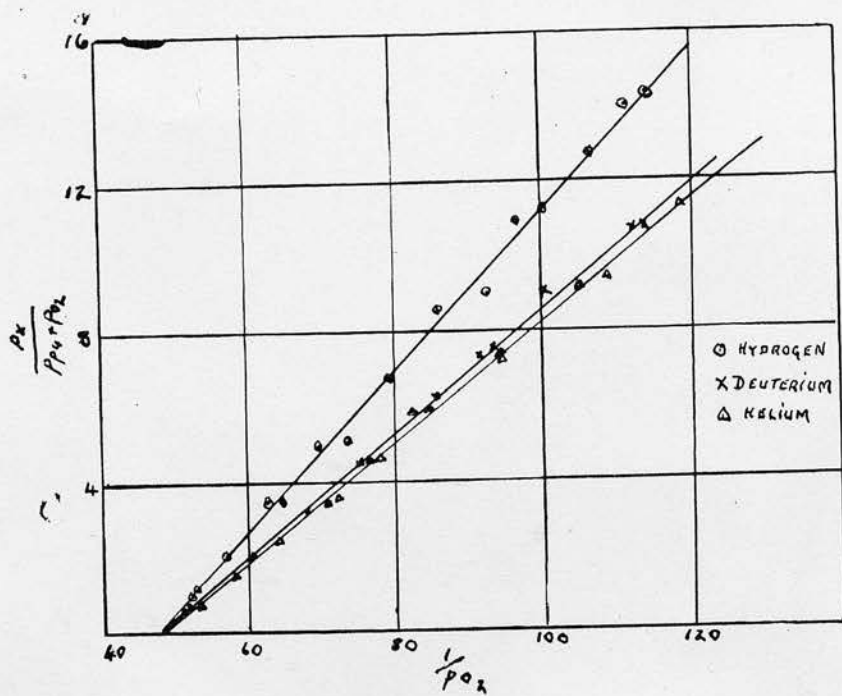


Fig. 2

The results tabulated above are summarised in fig. 2 where the reciprocal of the critical oxygen pressure p_{o_2} is plotted against the quantity $\frac{p_x}{p_{p^*} + p_{o_2}}$ for the three inert gases, hydrogen, helium and deuterium. It is seen that helium is only very slightly more effective than deuterium whilst they both have a much greater inert gas effect than hydrogen. From the slopes of the curves in Fig. 2 it was found that the ratio of the values of the inert gas factor for the three gases was given by $\mu_{H_2} : \mu_{D_2} : \mu_{He} = 1.00 : 1.30 : 1.32$.

The slope of the curve obtained by plotting $1/p_{o_2}$ against $\frac{p_x}{p_{p^*} + p_{o_2}}$ for hydrogen is nearer that for helium and deuterium than would be expected at first sight from theoretical considerations. But however if the number of assumptions and approximations made in deriving the expression for the inert gas factor μ_x (equation 20) is considered, these values obtained for μ_{H_2} , μ_{D_2} and μ_{He} are quite within reason. The difficulty in deriving theoretically an expression for μ for an inert gas lies in the fact that it is necessary to consider the problem of the diffusion of two chain carriers, alternately disappearing and reappearing during development of the chain, into a ternary gas mixture. 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 for the inert gas factor

$$\text{i. e. } \mu_x = \frac{G_{AX}^2 \left(\frac{1}{M_A} + \frac{1}{M_M} \right)^{\frac{1}{2}}}{G_{AM}^2 \left(\frac{1}{M_A} + \frac{1}{M_X} \right)^{\frac{1}{2}}} \quad (20)$$

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. Semenoff²⁰ assumes that one of the chain carriers is an oxygen atom (or less likely an activated oxygen molecule²¹) and the other some lower oxide of phosphorus of the type P_4O_n . If this view is correct then M_A the mean molecular weight of the chain carriers will have a minimum value of roughly seventy so that when the inert gases, hydrogen deuterium, helium are used $\frac{1}{M_A}$ will be very small in comparison with $\frac{1}{M_X}$ and hence may be neglected. Now as the molecular diameters of hydrogen and deuterium^{16 17} are the same then

$$\frac{\mu_{D_2}}{\mu_{H_2}} = \sqrt{\frac{M_{D_2}}{M_{H_2}}} = \sqrt{2} \text{ a somewhat higher value than that obtained experimentally.}$$

But however it has been suggested from results obtained by Melville and Ludlam³⁵ in experiments carried out with a tungsten filament, that the rate of starting of chains in the P_4-O_2 reaction may be proportional to $P_{P_4}^{\frac{1}{2}}$, a suggestion which indicates the possibility of 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 P_2 molecules^{22 23} into oxygen, when the typical glow emitted from a P_4-O_2 explosion was observed. Furthermore, experiments described in the next part of the thesis indicate that, in all probability in the stable reaction below the lower limit, P_2 molecules are intimately connected with the initiation and development of chains. Whilst the evidence in support of P_2 molecules playing an important role 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 by the reaction in some way of the P_2 molecules with O_2 or P_4 molecules, which then results in the initiation and development of the chains, it is possible that one of the chain carriers is a P_2 molecule. In the event of this being true, M_A would have a value of approximately thirty-five so that $\frac{1}{M_A}$ cannot be neglected as before and $\frac{\mu_{P_2}}{\mu_{H_2}}$ would have a smaller value than $\sqrt{2}$ although not so low as to fully account for the experimental results.

INTRODUCTION

PART II.

Displacement of the explosion limits in phosphorus-oxygen mixtures by the action of ultraviolet light. Study of the photochemical initiation of the stable reaction between phosphorus vapour and oxygen.

I N T R O D U C T I O N .

The introduction of the conception of branching chains into the theory of thermal chain reactions, and of the deactivation of the chains either in the gas phase or on diffusing to the walls, has provided a suitable explanation for the mechanism of many oxidation reactions. While, in the main, experimental work has shown the essential similarity underlying these reactions, and hence supported the general theoretical equations characterizing chain formation, there are many corollaries to the theory which still require to be examined in detail.

One such corollary the truth of which is assumed in the derivation of expressions for the explosion limit is that the latter should be independent of the rate of starting of the chains, provided of course that some reaction, even although too small to measure, does take place. For according to Dalton and Hinshelwood¹³ the stationary concentration of one of the chain carriers

X_0 in the P_4-O_2 reaction is given by

$$[X_0] = \frac{k_1 k_2 [O_2] F(c) + k_1 K F(c)}{(1-\alpha) k_2 k_3 [P_4] [O_2] + k_2 K [O_2] + k_3 K [P_4] + K^2} \quad (21)$$

where k_1 , k_2 and k_3 are velocity coefficients, $[O_2]$ and $[P_4]$ concentrations of oxygen and phosphorus vapour respectively and K the rate of deactivation of X_0 at the walls. $k_1 F(c)$ is the initial rate of production of the chain centres whilst α introduces the condition that more than one molecule of X_0 can be produced from the other chain carrier X_p at collision, i.e. branching can take place.

It is seen that if α is greater than unity, the first term in the denominator of the above equation may have a sufficiently large negative value to be greater than the rate of deactivation term $[k_2 K [O_2] + k_3 K [P_4] + K^2]$ so that the rate of production of new chains owing to the occurrence of branching will be greater than the rate at which they are terminated. Hence no stationary state is possible and explosion will take place. At explosion however $[X_0]$ will be infinitely great so that the condition for explosion is that

$$(1-\alpha) k_1 k_3 [P_4] [O_2] + k_2 K [O_2] + k_3 K [P_4] + K^2 = 0 \quad (22)$$

As the term $F(c)$ does not appear in the denominator it follows therefore, 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 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,²⁴ thermally²⁵ electrically,²⁷ oxygen²⁸ atoms, and chlorine²⁸ atoms all reduce the temperature of spontaneous ignition of H_2-O_2 mixtures, whilst at

temperatures approximating to room temperature conditions simulating a lower explosion pressure can be obtained by using a spark to start the chains.²⁹ 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 H_2 , CO , and CH_4 by nitrogen peroxide. A similar alteration in the explosion limits in the oxidation of carbon bisulphide,³⁰ sulphur³¹ 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. their explosion limits are influenced by temperature changes and explosion takes place at fairly high temperatures. The situation may be summarized 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 partially dependent on the rate of initiation. Thus to express completely the condition for explosion some temperature dependent factor should be introduced.

With phosphorus and phosphine however the propagating collisions are almost a 100% efficient, so that

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 that 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 probability of branching and the probability 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 the introduction of active centres into P_4-O_2 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.^{32 33} Melville,³⁴ however, showed that the displacement of the lower limit was due to a change in the condition of the walls.

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

$$\omega = \frac{n_0}{1-\alpha} \quad (23)$$

where n_0 is the number of initial centres and α the average number of elementary reactions entailed by one

given reaction i.e. the probability of the continuation of the chain.

Under ordinary conditions n_0 is so small that the rate of reaction outside the explosion limits is so low as to defy detection by experimental methods. If however by increasing n_0 , the rate of production of the chains is raised sufficiently it should be possible to observe and investigate the kinetics of a stable reaction outside the explosion limits. Thus the introduction of active centres into P_4-O_2 mixtures may lead to two results:-

- (1) it may produce a displacement of the explosion limits
- and (2) it may initiate a stable oxidation reaction outside these limits.

There are two easily controllable methods of introducing active molecules into a gaseous system without raising the temperature as a whole viz. by a hot filament and photochemically.

Melville and Ludlam³⁵ have succeeded by heating filaments of tungsten and platinum in P_4-O_2 mixtures, in initiating and observing the kinetics of the oxidation reaction below the lower limit. Their results can be summarised in the following equation:-

$$-\frac{dp}{dO_2} = K p_{O_2} p_{P_4} \left(1 + \frac{\mu P_4}{p_{P_4} + p_{O_2}} \right) d^2 e^{-\frac{U}{RT}} \quad (24)$$

where p_{O_2} , p_{P_4} and p_x are the pressures of oxygen, phosphorus vapour, and inert gas respectively: d is the diameter of the vessel, μ a constant depending on the nature of the inert gas, and $U = 16$ K cal. It was decided to use the optical method, as the active molecules are produced in the gas phase itself whereas by the filament method, active molecules may or may not be produced in the gas phase depending on whether the reactants after collision with the surface leave the surface or remain on it.

Thus by producing, optically, active centres in P_4-O_2 mixtures outside the explosion limits it was hoped

(i) to test the statement that the explosion limits should be independent of the rate of initiation of chains.

(ii) to produce the stable reaction below the lower limit, to determine the kinetics of the same reaction and if possible show the correlation between the kinetics at and below the explosion limit.

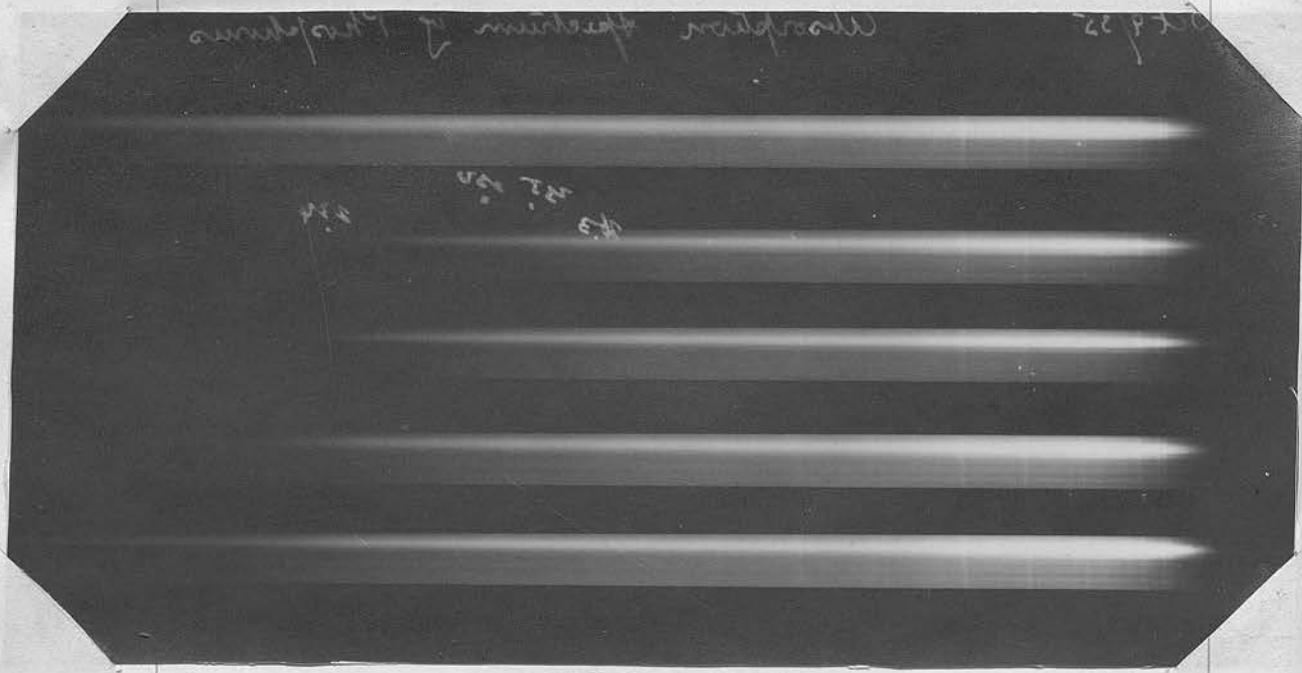


Fig. 3.



Fig. 4.

EXPERIMENTAL

Before proceeding to the main problems it was decided to photograph the absorption spectrum of phosphorus vapour using a continuous source of radiation. The source of light was a water cooled hydrogen tube consuming about 2 KW. The absorption vessel consisted of an evacuated fused silica tube about 15 cms. long, attached to which was a small tube containing purified white phosphorus, the whole apparatus being enclosed in a small furnace so that by altering the temperature of the furnace different pressures of phosphorus could be obtained. The exposures ranged from 5 mins. to 40 mins.

A series of exposures of 20 minutes was made at temperatures ranging from 18°C (pressure of phosphorus 0.021 mm. Hg) to 130°C (pressure phosphorus 29.65 mm. Hg). It is evident from Figs. 3 and 4 that definite absorption takes place in the region of the mercury line at 2537, heavy absorption at 210, the group of strong zinc lines. Oxygen on the other hand does not begin to absorb until beyond 200. It was obvious that

suitable sources of illumination would be zinc and aluminium sparks. The sparks were fed from a 10 KVA 6600 volt transformer with suitable condensers across the secondary. The electrodes were kept cool by a strong blast of air.

The apparatus used was the same as in the previous section, except for the fact that during the preliminary experiments the reaction vessel consisted of a cylindrical silica vessel about 15 cms. long and 2 cms. diameter. Oxygen entered the vessel through the capillary C, and by rotating the two way tap T_1 through 180° the flow could be instantly arrested. Calibration of the rate of flow of the oxygen was carried out as in the previous section. The inert gases were introduced into the reaction vessel by means of T_3 which was made in the form of a gas pipette, and the pressures were measured on the oil manometer M, which was shut off during experiments to prevent slight solution of the gases in the oil.

White phosphorus was prepared in the usual manner its pressure being regulated by immersing the phosphorus reservoir in thermos flasks containing mixtures of ice and water.

Oxygen was obtained from cylinders and dried by passing it slowly through a liquid air trap before storing in the oxygen reservoir O. Nitrogen was freed from the oxygen it contained (0.5%) by passing it over

heated copper and then through liquid air traps. The argon used contained 0.5% nitrogen but was oxygen free.

The method employed made use of the known critical oxidation pressure. It consisted in adding a known amount of oxygen to the phosphorus vapour, illuminating this mixture with light from the zinc spark, for a given length of time and then determining how much oxygen had to be added to bring the pressure up to the critical oxidation pressure. The difference between the total oxygen pressure for those mixtures where illumination had been effected, and the normal explosion pressure gave a means of determining whether any oxidation of the phosphorus or displacement of the lower limit had taken place.

The actual procedure was as follows:-

(a) With taps T_5 , T_4 , T_3 and T_2 shut (Fig. 1) oxygen was allowed to leak through the capillary into R which contained phosphorus at the desired pressure and the explosion time t_1 noted.

(b) The flow of oxygen was stopped, R pumped out and then filled with phosphorus vapour at the desired pressure.

(c) Oxygen was then allowed to leak into R for the requisite length of time t_2 , (t_2 being less than t_1) when tap T_1 was rotated quickly through 180° and the flow instantly arrested.

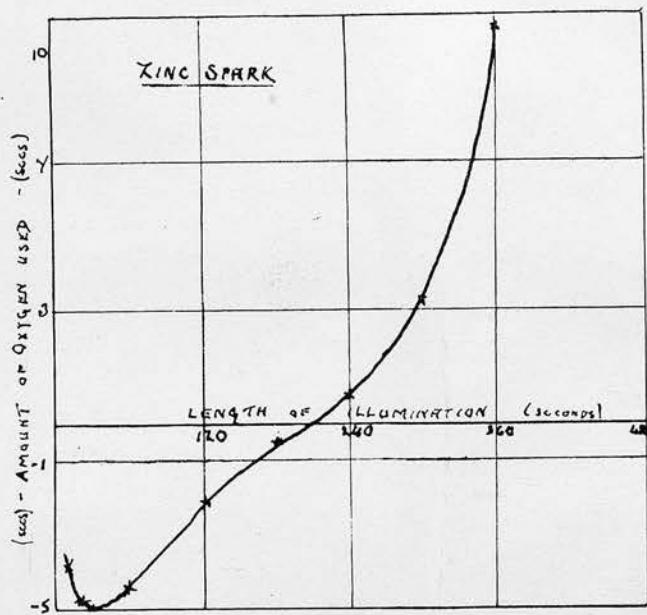


Fig 5

(d) After illuminating the mixture for the desired length of time with light from the zinc spark, the flow of oxygen was restarted and the time t_3 taken for explosion to occur determined.

The difference between the normal explosion pressure t_1 , and the total oxygen pressure ($t_2 + t_3$) for those mixtures which had been illuminated showed whether any displacement of the lower limit or oxidation of the phosphorus had taken place. The rate of flow of oxygen through the capillary was checked after every set of readings and the mean of two such checks used to find the absolute pressures of oxygen. But however, seeing that the flow of oxygen through the capillary remained constant, the pressures in the majority of cases are conveniently expressed in the equivalent number of seconds. In carrying out experiments conditions were standardised as far as possible.

Results: -

Table 4 shows a typical set of results obtained in the preliminary investigation of the action of ultra-violet light on P_4-O_2 mixtures. During this set of experiments 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.

In Fig. 5 the total pressure of oxygen ($t_1 + t_2$) is

plotted against length of illumination.

Table No 4

Zinc Spark. Temperature of phosphorus reservoir = 0°C
 Temperature of reaction vessel = 16°C.
From Calibration curve 1 second $\equiv 3.86 \times 10^{-4}$ mms. Hg.

Length of Illumination. (secs.)	Initial Concentration of Oxygen. t_1 (secs)	Time for Explosion t_2 (secs.)	Total Pressure of Oxygen (t_1+t_2) secs.	Amount of Oxygen used up. (secs.)
0	0	98.8	98.8	-
360	82.5	26.9	109.4	10.6
300	82.5	19.6	102.1	3.3
240	82.5	17.0	99.5	0.7
180	82.5	15.7	98.2	-0.6
120	82.5	14.2	96.7	-2.1
60	82.5	11.9	94.4	-4.4
30	82.5	11.3	93.8	-5.0
20	82.5	11.4	93.9	-4.9
10	82.5	12.4	94.9	-3.9
1200	82.5	45.2	127.7	+28.9
0	0	98.8	98.8	-

The last column of Table 4 shows the difference between the pressures of oxygen required for explosion of illuminated mixtures of phosphorus vapour and oxygen and for explosion of similar non-illuminated mixtures.

From Fig. 5 it is seen that for exposures of 180 secs. duration and less the total pressure of oxygen required for explosion was less than the normal explosion pressure of a similar mixture. Evidently the mixture had on illumination become more susceptible to explosion, thus resulting in a lowering of the critical pressure.

It was obvious therefore that illumination of P_4-O_2 mixtures with ultraviolet light produced two effects simultaneously in the mixture viz:

(i) It caused explosion to take place in the mixture at lower pressures than the normal explosion pressure, and (ii) initiated the oxidation of phosphorus at pressures below the lower limit.

By using suitable conditions obtained by altering the intensity of the light and length of exposure, it was found possible to treat the above two effects from the practical point of view as two independent phenomena.

I Effect of ultraviolet light on the explosion limits in P_4-O_2 mixtures.

During the following series of experiments the length of exposure of the P_4-O_2 mixtures to ultraviolet light was cut down to 15 seconds and the intensity of light reduced so that very little photo-oxidation occurred. The actual experimental procedure differed very little from the procedure in the previous experiment.

(1) Phosphorus vapour was let into R - the reaction vessel - until the desired pressure was obtained. Oxygen was allowed to leak through the capillary until the pressure in the reaction vessel was just below the explosion pressure. The flow of oxygen was then stopped and the mixture illuminated for 15 seconds. The flow of oxygen was restarted and the time for explosion noted. The difference between the time taken in the case of a non-illuminated mixture and the explosion time for an illuminated mixture was a measure of the displacement of the lower limit by the ultraviolet light.

(2) Different intervals of time (t) between the cessation of illumination and the occurrence of explosion were allowed to elapse 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.

In later experiments the zinc spark was replaced by a mercury vapour lamp which was found to be more suitable for the work. Care was taken to exclude all mercury vapour from the reaction vessel so that no photosensitization could take place.

Results.

Tables 5 and 6 show the results obtained by illuminating for 20 secs. the P_4-O_2 mixtures with light from the zinc spark and mercury arc (respectively). The

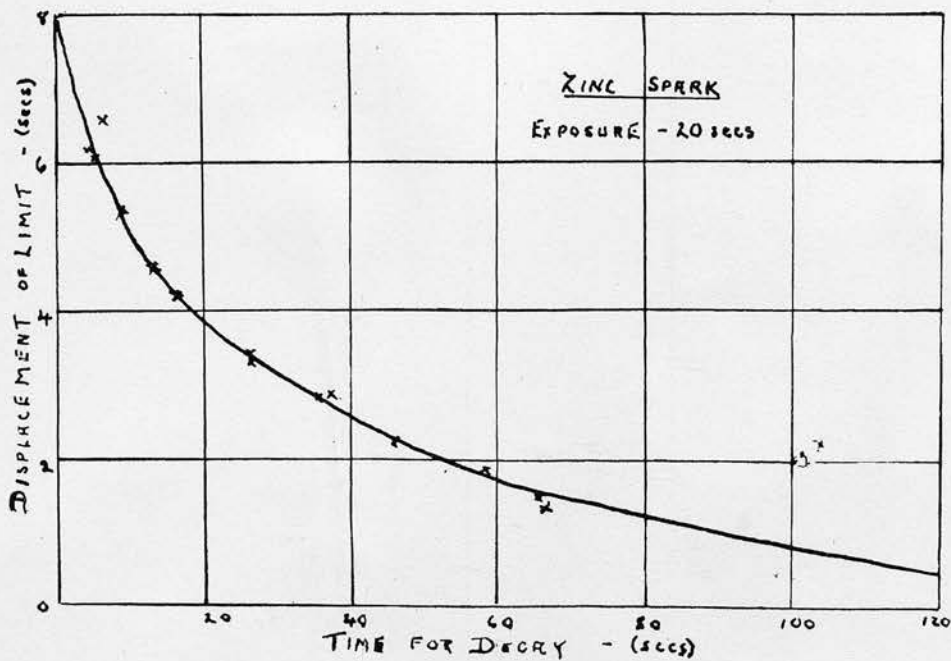


Fig 6

pressures of oxygen are expressed in seconds. The amount of lowering of the critical limit was plotted against t the time for decay, giving the decay curve Fig. 6.

Table No 5

Zinc Spark

Temp. of Phosphorus = 0°C.

From calibration curve 1 sec. = 7.1×10^{-4} mms. Hg.

Exposure: - 20 secs.

Explosion Pressure. No Illumination (secs.)	Time for Decay. t (secs.)	Explosion Pressure after Illumination (secs.)	Lowering of Limit after time t (secs.)
70.3	65.8	68.8	1.5
70.6	55.0	68.1	2.5
69.2	46.3	66.9	2.3
69.6	36.0	66.7	2.9
70.5	27.0	67.1	3.4
70.8	16.8	66.6	4.2
70.8	5.1	64.8	6.0
70.5	4.7	64.4	6.1
70.4	9.5	65.0	5.4
70.9	6.6	64.3	6.6
70.5	26.9	67.1	3.4
71.0	37.8	68.1	2.9
71.2	48.4	68.7	2.5
70.8	58.9	68.9	1.9
71.0	66.7	69.7	1.3
70.9	66.9	69.9	1.0

In the following table the results marked A were obtained in a clean reaction vessel whilst set 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.

Table No 6

Mercury Arc

Temp. of Phosphorus = 0°C.

From calibration curve 1 sec. $\equiv 6.9 \times 10^{-4}$ mms. Hg.

Exposure 15 secs.

	Normal Explosion Pressure T (secs.)	Time for Decay t (secs)	Initial Conc. of Oxygen (T secs)	Time for Explosion (T secs.)	Lowering of Limit T-(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

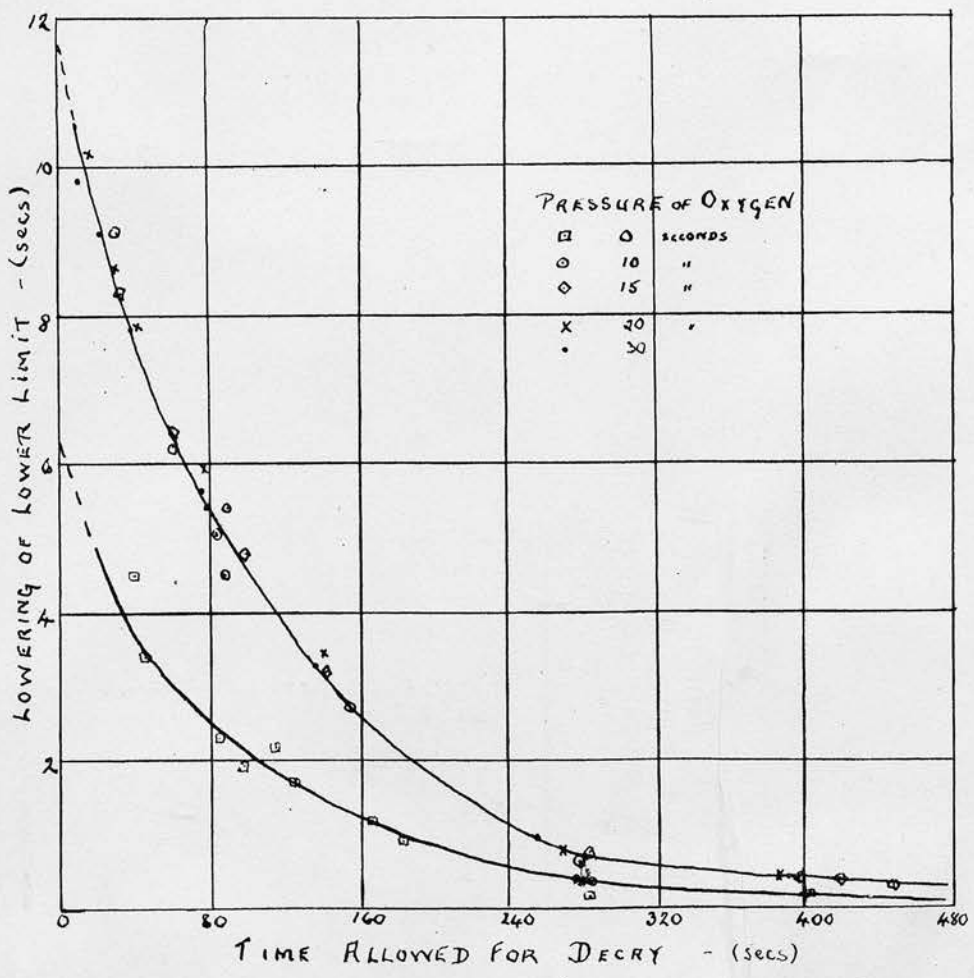


Fig 7.

Other series of experiments are given in tables 7-11 where the length of exposure and pressure of phosphorus vapour was kept constant, whilst the pressure of oxygen varied from zero to a pressure 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 to that used in the preliminary investigation.

Table No 7

Mercury Arc

Temp. of Phosphorus = 0°C.

Calibration curve 1 sec $\equiv 5.78 \times 10^{-4}$ mms. Hg.

Exposure 15 secs.

Initial Conc. of Oxygen (secs.)	Time for Explosion (secs.)	Total Oxygen required for Explosion	Displacement of Lower Limit (secs.)	Time for Decay (secs.)
0	47.6	47.6	-	-
0	44.2	44.2	3.4	45
0	45.3	45.3	2.3	86
0	45.9	45.9	1.7	127
0	46.4	46.4	1.2	168
0	46.9	46.9	0.7	289
0	47.3	47.3	0.3	450
0	43.0	43.0	4.6	43
0	45.6	45.6	2.0	76
0	45.3	45.3	2.3	115
0	46.7	46.7	0.9	189
0	47.5	47.5	0.1	284
0	47.4	47.4	0.2	404
0	47.6	47.6	-	-

Table No 8Mercury Arc

Temp. of Phosphorus = 0°C.

From calibration curve 1 sec. $\equiv 5.78 \times 10^{-4}$ mms. Hg.

Exposure 15 secs.

Initial Conc. of Oxygen (secs.)	Time for Explosion (secs.)	Total Oxygen Pressure (secs.)	Displacement of Lower Limit (secs.)	Time for Decay (secs.)
10.0	37.5	47.5	-	-
10.3	32.7	43.0	4.5	90
10.2	28.2	38.4	9.1	30
10.4	30.9	41.3	6.2	62
10.4	32.3	42.7	4.8	93
10.2	34.5	44.7	2.8	156
10.2	36.7	46.9	0.6	279
10.2	36.9	47.1	0.4	398
10.0	37.5	47.5	-	-

Table No 9Mercury Arc

Temperature Phosphorus = 0°C.

From Calibration curve 1 sec. $\equiv 5.78 \times 10^{-4}$ mms. Hg.

Exposure 15 secs.

Initial Conc. of Oxygen (secs.)	Time for Explosion (secs.)	Total Pressure of Oxygen (secs.)	Displacement of Lower Limit (secs.)	Time for Decay (secs.)
15.0	32.5	47.5	-	-
15.1	24.1	39.2	8.3	34
15.0	24.6	39.6	7.9	40
15.0	26.1	41.1	6.4	61
15.0	27.1	42.1	5.4	90
15.3	28.9	44.2	3.3	145
15.3	29.9	45.2	2.3	205
15.0	31.6	46.6	0.9	327
15.3	31.8	47.1	0.4	420
15.2	32.3	47.5	-	-

Table No 10Mercury Arc

Temp. of Phosphorus = 0°C.

From calibration curve 1 sec $\equiv 5.78 \times 10^{-4}$ mm. Hg.

Exposure 15 secs.

Initial Conc. of Oxygen (secs.)	Time for Explosion (secs.)	Total Oxygen Pressure (secs.)	Displacement of Lower Limit (secs.)	Time for Decay (secs.)
20.2	27.5	47.7	-	-
20.3	17.2	37.5	10.2	17
20.0	19.1	39.1	8.6	30
20.0	19.8	39.8	7.9	42
20.0	21.8	41.8	5.9	77
20.0	24.2	44.2	3.5	145
20.0	26.9	46.9	0.8	270
20.3	27.0	47.3	0.4	387
20.2	27.5	47.7	-	-

Table No 11Mercury Arc

Temp. of Phosphorus = 0°C.

From calibration curve 1 sec. $\equiv 5.78 \times 10^{-4}$ mm. Hg.

Exposure 15 seconds.

Initial Conc. of Oxygen (secs.)	Time for Explosion (secs.)	Total Oxygen Pressure (secs.)	Displacement of Lower Limit (secs.)	Time for Decay (secs.)
30.4	17.9	48.3	-	-
30.4	18.1	38.5	9.8	8.1
30.3	8.9	39.2	9.1	22
35.0	5.0	40.0	8.3	15
35.0	5.4	40.4	7.9	25
30.4	9.1	39.5	8.8	40
35.1	6.8	41.9	6.4	37
30.3	12.4	42.7	5.6	75
35.0	7.9	42.9	5.4	78
30.3	14.7	45.0	3.3	138
30.3	17.0	47.3	1:0	257
30.3	17.6	47.9	0.4	378
30.2	18.0	48.2	0.1	500
30.4	17.9	48.3	-	-

The results obtained show definitely that mixtures of phosphorus vapour and oxygen at pressure 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. This effect however is not permanent but decays slowly with time, the original explosion pressure being very nearly reached after allowing the illuminated mixture to stand for five to six minutes after cessation of illumination. Fig. 6 shows that the rate of decay and amount of displacement of the lower limit evidently depended to some extent on the condition of the walls as the rate of decay for a clean vessel differed considerably from that for one which had been in use a considerable period of time. It is seen from Fig. 7 that although the rate of decay and amount of lowering is independent of the pressures of oxygen, the amount of lowering of the explosion limit differed considerably from that obtained when no oxygen at all was present in the reaction vessel and only phosphorus vapour was exposed to illumination.

There are two possible explanations of the occurrence of the lowering of the explosion limit by the ultraviolet light. Illumination of the P_4-O_2 mixtures may result in the formation in the gas phase of some active substance with an appreciable time of survival. The

formation of active molecules of this substance could only result in 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 that 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 that such a molecule, if produced, would be active in virtue of the chemical unsaturation rather than its high energy content.

On the other hand, however it is more likely on account of the low rate of decay that the displacement of the lower limit is due to a change in the surface of the walls rather than to the production of active centres in the gas phase. It will be remembered that the concentration of one of the chain carriers X_0 in the P_4-O_2 reaction is given by¹³

$$[X_0] = \frac{k_1 k_2 [O_2] F(c) + k_1 K F(c)}{(1-\alpha) k_2 k_3 [P_4] [O_2] + k_2 K [O_2] + k_3 K [P_4] + K^2} \quad (25)$$

where k_1 , k_2 and k_3 are velocity coefficients, $[O_2]$ and $[P_4]$ concentrations of oxygen and phosphorus respectively, K the rate of deactivation of X_0 on the walls, and $k_1 F(c)$ the rate of production of the chain centres.

$(1-\alpha)$ is the term introduced to account for the occurrence of branching. The condition for explosion is that $X_0 = \infty$ so that the denominator of ⁽²⁵⁾ equals zero. $F(c)$ does not occur in the denominator so that the explosion pressure should be independent of the rate of production of the chain centres. Now the propagating collisions in the P_4-O_2 reaction as in the PH_3-O_2 ¹³ reaction are almost 100% efficient so $k_2 = k_3$. Also since k_2 is large K^2/k_2 is probably very small and therefore may be neglected. Introducing these simplifications into equation (25) and equating the denominator to zero we have

$$(\alpha-1) k_3 [P_4] [O_2] = K [[P_4] + [O_2]] \quad (26)$$

so that

$$[P_4] [O_2] = K' \times \text{constant}$$

where K' expresses the efficiency of the deactivating collisions of X_0 with the walls. K' will depend therefore on the surface of the walls so that an alteration in the surface of the walls of R on illumination may result in an alteration in K' and consequently give rise to a displacement of the explosion limit. It was necessary therefore to examine the lowering effect with a view to deciding whether the displacement of the lower limit 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 following experiments were carried out in order to decide definitely the question whether the effect was due to a change in the condition of the walls or not. But although it is extremely likely that it is a wall effect it does not necessarily follow that the lowering is due merely to a decrease in the efficiency of the deactivating collisions with the walls. Assuming that initiation of the chains occurs on the walls¹² themselves, the displacement of the lower limit may result from the formation, on the walls, of a number of active molecules or atoms capable of initiating the chains. This question however and the significance of the results shown graphically in Fig.7 will not be discussed until later.

Experimental.

The principle of the method employed, for the purpose of deciding whether the lowering effect was a wall effect or was due to some change in the gas phase, consisted in illuminating a mixture of phosphorus vapour and oxygen in one vessel and then immediately transferring it to a second vessel similar in all respects where the explosion pressure is measured. If the effect is a surface effect then the explosion pressure in the second

vessel 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 the second vessel a diminished explosion pressure.

The actual apparatus is shown in Fig.8. A and B were two similar silica tubes of 11 cms. length and 1.5 cms. diameter fitted with the taps T_1 and T_5 respectively. They were connected to each other by a short length of tubing and also to the reservoir containing white phosphorus and C the capillary leading to the oxygen reservoir. T_4 was a two way tap used for starting and stopping the flow of oxygen through the capillary. By opening T_1 or T_5 it was possible to connect A or B with the phosphorus and oxygen reservoirs as desired. B was also connected through the tap T_6 directly to the pumps for it was found that if the gases were not pumped through the reaction vessel difficulty was experienced in obtaining a constant explosion pressure.

The lower portion of A passed through the stopper of a sealed mercury reservoir and dipped well under the surface of the mercury. The single limb of a two way tap T_2 also passed through the cork into the air space above the mercury, one of the other two limbs being attached to a suction pump the other being drawn down to a fairly fine jet. By altering the position of the

two way tap it was possible therefore, to remove air from or allow air to enter the air space above the mercury so that the level of the mercury in A could be altered rapidly at will.

Now although the use of mercury as a means of transferring the reaction mixture from one vessel to another added a further complication in that mercury photo sensitization probably would and in fact did take place (the rate of the stable oxidation reaction was found to increase very considerably) it was found to be the only suitable medium for the purpose. Phosphoric acid was tried and found to be impracticable. To get over this difficulty to some extent it was decided therefore to fill A with phosphorus vapour only and then illuminate it with light from the mercury arc, transfer to B and find the explosion pressure. This procedure was assumed to be a legitimate one for

(a) the absorption of light by oxygen only becomes significant at much lower wavelengths of light than those used (< 200) so that the origin of the lowering effect must be in the absorption of light by the phosphorus vapour that is in the activation of the phosphorus molecule.

(b) Fig.7 shows that the rates of decay for illumination of the phosphorus vapour alone and of mixtures of phosphorus vapour and oxygen are the same. So it appear-



ed very likely that the decay of the lowering effect was the result of a change in nature or condition of the same substance in both cases. ~~or~~ If not it is almost certain to be of the same type that is either wall or gas effect.

The actual experimental procedure was as follows: - Before commencing experimental work phosphorus vapour and oxygen were allowed to combine explosively in both A and B so that the condition of the walls would be the same for both vessels. A and B were both pumped out and the level of the mercury in A adjusted to a definite mark S. Taps 3, 5 and 6 were then closed and A filled with phosphorus vapour to the desired pressure by opening T₇. After shutting off the phosphorus reservoir and opening T₅ the phosphorus vapour was transferred to B by allowing air to enter the mercury reservoir so that the mercury level in A rose until it reached the tap T₁ which was then closed. The flow of oxygen was immediately started and the time taken for explosion to occur noted. From previous calibrations this time could be converted into pressures of oxygen expressed in mms. of mercury if so desired.

After explosion A and B were then pumped out - the level of the mercury in A being lowered to the original level - and the whole procedure repeated with the addition that after filling A with phosphorus vapour it was

exposed to light from a water cooled mercury lamp before transfer to B where the explosion pressure was measured.

In order to show that the normal lowering effect was occurring in A - the explosion pressures of similar mixtures of P_4 and O_2 with and without illumination were found. Conditions during these experiments were kept as far as possible, the same, and the time for transfer kept as short as possible (approx.) 15 secs. so that no error due to decay of the lowering effect could occur.

Table No 12.

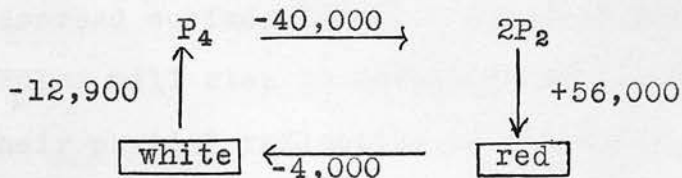
<u>Mercury Arc.</u>			Explosion time in A = 54.2 secs.		
No Illumination in A	Illumination in A	Explosion in B	Illumination in A	Explosion in B	Illumination in A
		Explosion in B			Explosion in A
56.9		56.9	57.1		51.0
57.5		57.5	57.0		53.0
56.8		56.8	56.6		51.2
57.0		57.0	56.9		50.7

It is seen that although illumination of a P_4-O_2 mixture in A results in a displacement of the explosion pressure, 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 shows quite definitely that illumination of the P_4-O_2 mixtures below the lower limit results in a change having been produced in the surface conditions of the reaction vessel. This alteration of the surface conditions gives rise to a displacement of the lower explosion limit, which may be due to either 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 ultraviolet, the original cause of the lowering effect must lie in the absorption of the light by the phosphorus molecules.

During all these experiments it was found that a deposit of red phosphorus was formed on the walls after illumination for a considerable period of time had taken place. In connexion with this Melville³⁴ and Gray³⁶ have shown that the mechanism for the production of red phosphorus 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 as red phosphorus was deposited as a result of the absorption of light by phosphorus molecules, it follows that dissociation of the phosphorus molecules 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 Gray³⁶ found, when investigating the transformation of white phosphorus to red phosphorus by means of a heated filament, that red phosphorus was deposited not only on the walls of the reaction vessel opposite the filament, but also in parts of the apparatus well away from the source of the dissociation. It was obvious therefore that reflection of the P_2 molecules by the walls could and did occur, so that they had a small but definite time of survival. This experimental 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 by the light 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, owing to their partial reflection by the walls, they can exist

for a considerable length of 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 ceased. Investigation of the effect of surface conditions on the lower explosion limits^{37 38 39} in many chain reactions have shown that in all cases the lower limit is extremely sensitive to changes in the condition of the walls. In connexion with this it is worth noting that after cleaning and drying the reaction vessel it was found that 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 Garner⁴⁰ and Coslett 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 the reflecting power of the walls. This, by increasing the length of the chains would result in a lowering of the explosion pressure.

It has been shown (Fig.7) that the displacement of the lower limit was much greater when mixtures of phosphorus vapour and oxygen are illuminated than when phosphorus vapour alone was used. But although the displacement was increased by the presence of oxygen, it

was shown to be independent of the oxygen pressure. This immediately suggested that phenomenon was a surface effect and led to a possible explanation for it. Illumination of P_4-O_2 mixtures by ultraviolet light will produce, both in the gas phase and on the walls, P_2 molecules. These molecules 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 at the walls of molecules of some lower oxide of phosphorus. 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. The existence of these active oxide molecules 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 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 due partly to their combination to form red phosphorus

and also 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 ultraviolet light.

This explanation is however only advanced tentatively as there is no quantitative treatment of the problem 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 system by the ultraviolet light. In view of the fact that illumination of P_4-O_2 mixtures under identical conditions as used above results in a little oxidation of the phosphorus vapour occurring, this explanation although contradictory to the predictions of the theory of chain reaction is quite feasible. In this case, dissociation of the P_4 molecules into P_2 molecules by the ultraviolet 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.

In conclusion, it is clear that until a quantitative method of distinguishing between the effect of altering the rate of deactivation of the chain carriers and of altering the rate of initiation of the chains is possible, suggestions as to the cause of the displacement of the lower limit must be regarded as more or less speculative, awaiting experimental evidence of their validity.

Influence of ultraviolet light on the upper explosion limit of the P_4-O_2 reaction.

Although the problem of the upper explosion limit still awaits a full theoretical elucidation, two suggestions have been put forward to explain its existence. It has been shown that wall effects at the upper limit are negligible, so that deactivation of the chain carriers by the walls is no longer of any importance.

Kowalsky^{41 42} recognising this suggested that rupture of the reaction chains takes place in the gas phase and is due to small traces of impurities always present in oxygen. These traces of impurities were supposed to act in a similar manner to that of oxygen in the Hydrogen-Chlorine⁴³ reaction. It is interesting to note in this respect, that the position of the upper limit has been shown to be extremely sensitive to traces of some specific substances.

The theory accepted now is due to Dalton⁴⁴ who showed in his investigation of the oxidation of phosphine—a reaction similar to the P_4-O_2 reaction in that it exhibits two limits of inflammation, that the lower oxidation limit conformed to the expression

$$p_{PH_3} \cdot p_{O_2} \left(1 + \frac{A p_x}{p_{PH_3} + p_{O_2}} \right) d^2 = \text{constant}$$

except that the relation between $p_{P_{H_3}}$ and p_{O_2} was not strictly hyperbolic. This effect was ascribed to the rupture of the reaction chains in the gas phase, probably due to triple collisions between an active centre and two molecules of oxygen. Such an effect would of course be more noticeable with phosphine than with phosphorus since the total explosion pressure of a 1:1-mixture of phosphine and oxygen is 2 mms. (approx.) in a 2 cm. tube whilst for a corresponding mixture of phosphorus vapour and oxygen it is only about 0.05 mms. As the pressure increases deactivation in the gas phase becomes more and more pronounced and deactivation by the walls becomes less important until finally pressures are reached where wall deactivation becomes negligible.

Thus the upper pressure limit of the P_4-O_2 reaction depends on the balancing of two processes - 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. Now in the previous work where mixtures of phosphorus and oxygen at pressures below the lower critical pressure were exposed to ultraviolet light, active centres capable of initiating chains were introduced into the mixture in order to test the theory that the explosion limits should be independent of the rate

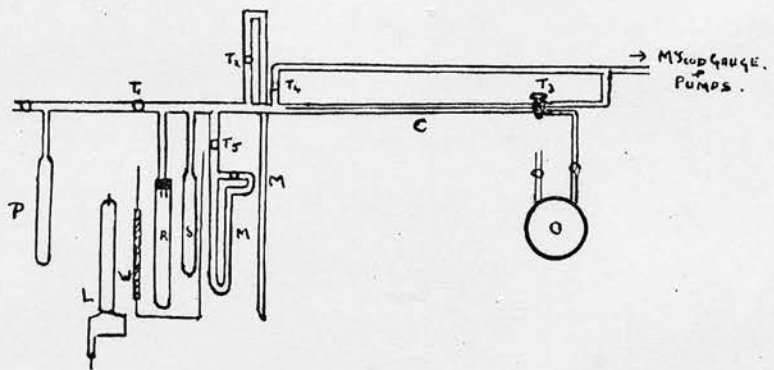


Fig. 9.

of initiation of the chains. Although displacement of the lower limit was obtained, it was shown that the latter may have been due to an alteration of the condition of the surface of the walls resulting in a decrease in efficiency of its power of deactivating the chain carriers, thereby giving rise to a lowering of the explosion limit.

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 the explosion limit. Hence any displacement of the upper limit obtained by exposing P_4-O_2 mixtures to light from a mercury arc must be due in some way to the production of active centres in the system and not to an alteration in the rate of deactivation of the chain carriers.

EXPERIMENTAL

The apparatus used for this part of the work was similar in form to that used in the experiments carried out at the lower limit. (Fig.9) The silica reaction vessel was replaced by a silica test tube R 8" x $\frac{3}{4}$ " which was cemented to the apparatus with 'Picene' wax. S was a glass reservoir in which, by immersing it in liquid air, phosphorus vapour could be condensed out. It was

shut off from the main phosphorus reservoir by the tap T_1 . As the pressures used were of the order of 200 mms. Hg, it was found necessary to thermostat the reaction vessel R, and the phosphorus reservoir S. The thermostat consisted of a metal box with a 6"x1" 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 found 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_2 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 - the lamp 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 until a pressure greater than the upper explosion pressure was reached. The liquid air was removed, and the reaction vessel and phosphorus reservoir was immersed in the

thermostat and allowed to stand for several minutes until the desired temperature was reached. The total pressure was read on the manometer. By opening the two way tap T_3 to the pumps the pressure in R was slowly lowered until finally explosion took place - the pressure being read off the manometer.

After pumping out R and S, the reaction vessel was again filled with phosphorus and oxygen in the same way as above, but in this case the pressure of oxygen was kept just above the upper explosion limit. The mixture was then exposed to illumination from the mercury lamp for a short time, and immediately after cessation of illumination R was viewed to see if explosion had occurred, whilst T_3 was opened to the pumps. The above procedure of illuminating P_4-O_2 mixtures at pressures just above the upper limit, shutting off the light and then viewing R to see if explosion had occurred, was the only method found suitable for testing the effect of ultraviolet light on the upper limit. For it was not possible to see any explosion occurring in R during illumination, and no difference in pressure or in the rate of decrease in pressure could be observed during illumination, so that exposure to the mercury lamp could not be carried out whilst pumping off the excess oxygen. The pressure of phosphorus vapour in R was obtained from the temperature of the thermostat.

RESULTS.

The results shown in table 13 are typical examples of the results obtained from a large number of experiments carried out in the above manner. Pressures of oxygen and phosphorus vapour are given in mms. of mercury.

Table No 13

Pressure of Phosphorus (mm. Hg)	Initial Pressure of Oxygen (mms Hg)	Pressure of Oxygen at which Explosion occurred	Experimental Conditions. Illumination
0.012	521	478	No
0.012	520	520	Yes
0.012	552	552	Yes
0.012	579	495	No
0.012	579	579	Yes
0.012	550	550	Yes
0.012	581	550	No
0.012	621	468	No
0.012	629	629	Yes
0.009	528	389	No
0.009	526	526	Yes
0.009	530	389	No
0.009	516	516	Yes
0.009	526	495	No
0.009	542	542	Yes
0.009	584	584	Yes
0.009	580	404	No
0.009	626	352	Yes
0.009	571	571	Yes
0.009	579	400	No

From the results obtained in the preliminary investigation tabulated above, it is seen that illumination of the reaction vessel causes a considerable dis-

placement of the upper limit towards higher pressures - a phenomenon which is 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 absorb the wavelengths of light used to any appreciable extent, these active centres must be some activated P_4 molecules, P_2 molecules, or more likely some phosphorus oxide molecules. These active centres or molecules 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 chain theory.

A possible explanation of the displacement lies in the tentative suggestion put forward by Melville and Roxburgh³³ to explain a similar displacement of the upper limit in the PH_3-O_2 reaction. They suggested that, as the upper limit is very sensitive to the stationary concentration of one of the chain carriers X_0 (so that obviously 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 large for the relationship to hold. The displaced limit will be therefore 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 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.

II The Stable Oxidation Reaction below the Lower Limit.

From the preliminary investigations on the effect of ultraviolet light on P_4-O_2 mixtures near the lower limit, it was seen (Table 4) that light from a zinc spark besides displacing the lower critical oxidation limit, also initiated a reaction between phosphorus and oxygen at pressures where under ordinary conditions no reaction could be observed. Experiments⁴⁵ have shown that a stable oxidation reaction, the kinetics^{13 34} of which show a very exact interrelationship with the kinetics of the explosive reaction, can be initiated by means of a mercury arc (photosensitised reaction) or by a zinc spark (direct reaction) below the lower limit in the oxidation of phosphine. Obvious experimental difficulties lay in the facts that (a) owing to the very small absorption of light by phosphorus vapour until far out in the ultraviolet, the 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 phosphorus pressure in the reaction vessel were impossible. It was decided however, to

carry out an investigation of the oxidation reaction and if possible, determine the kinetics of the reaction with the idea of showing the probable relationship between the course of the reaction at and below the lower limit. Furthermore it was thought likely that additional information on the initiation of the chains might be obtained.

Before proceeding however to a detailed investigation of the kinetics of the observed oxidation reaction, it was necessary to show that the reaction did possess the characteristics of a chain reaction. In this case the most suitable of all the criteria by which a chain reaction may be recognised was the study of the effect on the rate of reaction of the addition to the system of small quantities of inert gases. For, according to the chain theory of the kinetics of the oxidation of phosphorus at low pressures, the presence of an inert gas impedes the diffusion of the chains to the walls of the containing vessel and thus by increasing the chain-length results in a lowering of the explosion limit. It would be expected therefore that if the reaction now being investigated exhibits chain characteristics, then the addition of small quantities of gases such as argon and nitrogen should result in an acceleration of the rate of oxidation.

EXPERIMENTAL

The only difference in the apparatus used in this part of the work from that used for work on the lower limit (Fig.1), was that R the reaction vessel 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_{p_4} and p'_{O_2} respectively, for requisite lengths of time. 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 the inert gases argon and nitrogen, and the respective rates of oxidation in these cases compared. The pressure of inert gas was given by the oil manometer M, which was shut off from the reaction vessel during experiments, to prevent slight solution of the gases. Oxygen pressures were obtained by calibration of the rate of flow of the gas through the capillary in exactly the same manner as in previous experiments.

Now it was shown in the previous work, that illumination of a P_4-O_2 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, after illumination had ceased, for three to four minutes. In the following experimental work, the P_4-O_2 mixtures were allowed to stand after cessation of illumination for four minutes, 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 also experienced by the formation during illumination of a reddish brown deposit on the walls of the reaction vessel. This deposit, since it was easily removed by heating in which circumstances inflammation occurred, and also by treatment with bromine water, was shown 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. Care was

taken therefore to exclude all traces of mercury vapour from the reaction vessel, and the reacting gases (a liquid air trap was placed between the reaction vessel and the McLeod gauge in addition to that guarding the pumps) in order to prevent the possible occurrence of a photosensitized reaction.

The preparation and purification of phosphorus and oxygen was carried out in exactly the same way as in previous work. Nitrogen was freed from oxygen by passing it over copper foil heated to 350°C, and then through a liquid air trap. Argon contained 0.5% nitrogen but was free from oxygen.

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 ultraviolet light below the lower limit are given in tables 14 and 15. 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 mms. were added. The pressure of inert gas is given in mms. of mercury while that of oxygen is expressed by the time (in seconds) during which oxygen entered the vessel.

Table No 14Argon.

Mercury Arc. Pressure of Phosphorus = 0.004 mms. Hg.

From Calibration curve 1 second = 6.91×10^{-4} mms. Hg.

Initial Conc. of Oxygen (secs.)	Pressure of Inert Gas (mms. Hg)	Time for Explosion (secs.)	Amount of Oxygen used up. (secs.)	Length of Illumination (mins.)
0	-	71.1	-	-
0	0.028	54.4	-	-
36.3	-	39.8	5.0	3
36.3	0.028	26.3	8.2	3
0	-	71.0	-	-
0	0.057	43.8	-	-
36.5	-	39.7	5.2	3
36.4	0.057	18.1	10.7	3
0	-	70.5	-	-
0	0.027	55.2	-	-
36.3	-	39.6	5.4	3
36.3	0.027	26.0	7.1	3
0	-	71.0	-	-
0	0.057	43.7	-	-
36.4	-	39.6	5.0	3
36.4	0.057	18.3	11.0	3

Table No. 15Nitrogen

Mercury vapour lamp.

Pressure of Phosphorus = 0.004 mms. Hg.

From Calibration Curve 1 second = 6.91×10^{-4} mm. Hg.

Initial Conc. of Oxygen (secs.)	Pressure of Inert Gas (mms. Hg)	Time for Explosion (secs.)	Amount of Oxygen used up. (secs.)	Length of Illumination (mins.)
0	-	70.8	-	-
0	0.013	61.7	-	-
36.5	-	39.3	5.0	3
36.5	0.013	31.0	5.8	3
0	-	70.2	-	-
0	0.026	55.1	-	-
36.5	-	38.4	4.7	3
36.5	0.026	25.4	6.8	3
0	-	71.3	-	-
0	0.039	50.0	-	-
36.6	-	39.8	5.1	3
36.6	0.039	20.5	7.1	3
0	-	70.2	-	-
0	0.052	46.4	-	-
36.5	-	38.8	5.1	3
36.5	0.052	19.8	9.9	3

The above tables show definitely that the presence of an inert gas in a P_4-O_2 mixture results in an acceleration of the rate of oxidation below the lower limit thus showing that this reaction initiated by the ultra-violet light is a chain reaction. Argon is seen to have a slightly greater accelerating effect than nitrogen which is to be expected since the smaller mass and diameter of the nitrogen is 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 explosion¹² limits in the P_4-O_2 reaction has been satisfactorily worked out, 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 $F(c)$. Now since there is no appreciable absorption of radiation from a zinc spark by oxygen - absorption only begins to become significant at shorter wavelengths - only X_p will be formed spontaneously.



X_0 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_0 and phosphorus.

As the reaction takes place below the lower limit deactivation of X_0 and X_p occurs on the walls and it is assumed that the rates at which X_0 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 then it could easily be shown that the equation for the lower explosion limit would be

$$[P_4] \left[[P_4] + [O_2] \right] = \text{constant},$$

or

$$[O_2] \left[[P_4] + [O_2] \right] = \text{constant},$$

which is not in so 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:-

$$\frac{d[X_0]}{dt} = k_2[X_p][O_2] - k_3[X_0][P_4] - K[X_0] = 0 \quad (27)$$

$$\frac{d[X_p]}{dt} = F(c) + k_3[X_0][P_4] - k_2[X_p][O_2] - K[X_p] = 0 \quad (28)$$

Now

$$F(c) = K \left[[X_p] + [X_0] \right] \quad (29)$$

$$\therefore [X_0] = \frac{F(c)}{K} - [X_p]$$

and hence

$$[X_p] = \frac{k_3[P_4] F(c) + KF(c)}{k_2K[O_2] + k_3K[P_4] + K^2} \quad (30)$$

If the chain length is great $F(c)K$ 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

$$[X_p] = \frac{[P_4] F(c)}{K \{ [O_2] + [P_4] \}} \quad (30a)$$

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

$$[X_p] = \frac{[P_4] F(c)}{K'} \quad \text{if } [A] = 0 \quad (30b)$$

Now

$$-\frac{d[O_2]}{dt} = k_2[O_2][X_p] = \frac{k_2[O_2][P_4] F(c)}{K'} \quad (31)$$

If I is the intensity of the light absorbed, then for the direct reaction,

$F(c) \propto I [P_4]$ since the amount of absorption is very small.

$$\text{Hence } -\frac{d[O_2]}{dt} \propto \frac{k_2 [O_2] [P_4]^2 I}{K'} \quad (32)$$

RESULTS.

Table 16 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. The pressures of oxygen are expressed in seconds - one second being equivalent to 6.907×10^{-4} mms. 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 No 16

pressure of phosphorus (mms. Hg)	0.004	0.004	0.004	0.004	0.004
pressure of oxygen (seconds)	30.0	20.0	10.0	37.0	30.0

Length of illumination t (mins.)	Δp (secs.)	Δp (secs.)	Δp (secs.)	Δp (secs.)	Δp (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
$\frac{R}{O_2^2}$ —	0.011	0.010	0.016	0.013	0.012

Another series of experiments is given in table 17 in which the intensity of the light, and oxygen pressure were kept constant while the pressure of phosphorus vapour was varied. The pressures of oxygen are expressed again in seconds - one second being equivalent to 6.907×10^{-4} mms. of mercury. From the values obtained for $R/[P_4]$ and $t \times [P_4]$ where t is time taken for a pressure change of 5.27×10^{-3} mms. Hg to occur it is seen that the rate of reaction $-d[O_2]/dt$ is directly proportional to the pressure of phosphorus vapour.

Table No 17

Mercury vapour lamp

pressure of oxygen (secs.)	30.0	30.0	30.0	30.0	30.0	30.0
pressure of phosphorus (mms. Hg)	0.004	0.009	0.007	0.009	0.013	0.004

Length of illumination t minutes.	Δp (secs.)	Δp (secs.)	Δp (secs.)	Δp (secs.)	Δp (secs.)	Δp (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 — (mm. Hg)	0.55×10^{-3}	1.22×10^{-3}	0.88×10^{-3}	1.32×10^{-3}	1.72×10^{-3}	0.60×10^{-3}
$\frac{R}{[P_4]}$ —	0.14	0.14	0.13	0.15	0.13	0.15
time for $\Delta p = 5.27$ $\times 10^{-3}$ mm. Hg. t	11.6	4.8	6.3	4.5	3.6	12.0
$t \times [P_4]$ —	0.046	0.043	0.044	0.040	0.047	0.048

It is seen from an inspection of equation (32) that the rate of reaction should be directly proportional to the light intensity. Table 18 shows results obtained from a series of experiments in which the pressures of phosphorus vapour and oxygen were kept constant while the intensity of the light was varied. Variation in the light intensity was obtained by use of a carbon-tetrachloride-cyclohexane intensity⁴⁶ filter. Care was taken that the length of exposure was well within the time at which decomposition of the filter commences. The constancy of the values obtained for R/I shows quite definitely that the rate is proportional to the first power of the intensity.

Table No 18

Mercury Arc.

pressure phosphorus vapour - 0.007 mm. Hg.
pressure oxygen - 55.0 seconds.

Intensity I	Initial Rate of Oxidation R	$\frac{R}{I}$
1.0	8.0	8.0
0.71	5.7	8.0
0.46	3.5	7.7
0.26	1.9	7.3
1.00	7.7	7.7
0.71	5.9	8.3
0.46	4.1	8.9
0.26	2.0	7.7
1.00	7.7	7.7
0.71	6.0	8.4
0.46	3.8	8.3
0.26	2.1	8.0
1.00	7.9	7.9

From the practical results shown in tables 16, 17 and 18 it is seen that the kinetics of the stable oxidation reaction can be expressed by:-

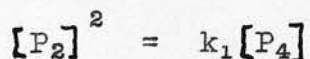
$$- \frac{d[O_2]}{dt} = R = [O_2]^2 [P_4] \times I \times \text{a constant} \quad (33)$$

The chain theory however, as is shown in equation 32, 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 between experimental results and theoretical deductions can be explained on the following lines, and is suggestive of a possible mechanism for the initiation of the chains. Although Semenov's^{11 12} theory indicates that the length of chains in the P_4-O_2 is proportional to the concentration of phosphorus molecules, he himself found experimentally¹⁰ that the chain length was proportional to the square root of the phosphorus concentration. This dependence of the chain length on the square root of the phosphorus concentration has been confirmed by Melville in his tungsten filament experiments,³⁵ and by other work on the P_4-O_2 reaction. It was suggested, also that the rate of starting of the chains was not proportional to the phosphorus concentration but to the square root of the concentration. Hence if the rate of initiation of the chains in the photochemical reaction is proportional to $[P_4]^{\frac{1}{2}}$ as the chain length is 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.

During these experiments red phosphorus was deposited on the walls of the reaction vessel. It has been shown by Melville, and Gray³⁶ that the production of red phosphorus from white phosphorus is due to the recombination of P_2 molecules at a surface. This suggests therefore that the ultraviolet light on illuminating a mixture of phosphorus vapour and oxygen causes a dissociation of P_4 molecules into P_2 molecules which can combine on the surface of the containing vessel. Later experiments have shown that illumination of phosphorus vapour with light from a mercury arc results in the production of red phosphorus. Furthermore illumination of P_4-O_2 mixtures in this manner results in a change in the condition of the surface of the walls of the containing vessel so that it appears extremely likely, (although it cannot be proved) that initiation occurs on the walls. Gray³⁶ has shown that initiation of chains in P_4-O_2 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 the molecules of some lower oxide of phosphorus leaving the surface which are capable of initiating chains in the gas phase. Before this however,

Semenoff had suggested that the production 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



this would account for the rate of initiation being proportional to the square root of the concentration of phosphorus 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 ultraviolet 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 the intensity of which is denoted by I will be given by

$$F(c) = I [O_2] [P_4]^{\frac{1}{2}} \times \text{constant}$$

not by

$$F(c) = I[P_4] \times \text{constant}$$

as indicated by theory. Hence, as the rate of reaction

$-d[O_2]/dt$ is given by

$$\frac{-d[O_2]}{dt} = \frac{k_2[O_2][P_4]^{\frac{1}{2}} F(c)}{K'} \quad (\text{page } 77)$$

$$\text{then } \frac{-d[O_2]}{dt} = [O_2]^{\frac{1}{2}} [P_4] I \times \text{a constant} \quad (34)$$

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 (tables 14 and 15) have shown that the presence of an inert gas resulted 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

$$P_{P_4} \cdot P_{O_2} \left(1 + \frac{P_x}{P_{P_4} + P_{O_2}} \right) d^2$$

where p_{P_4} , p_{O_2} , and p_x are the pressures of phosphorus vapour, oxygen and inert gas respectively and d is the diameter of the reaction vessel. If $f(p_{O_2}, p_{P_4})$ represents the rate of starting of the chains, then the rate of reaction $-d \frac{dp_{O_2}}{dt}$ will be expressed by

$$-\frac{dp_{O_2}}{dt} = K' f(p_{P_4}, p_{O_2}) \cdot p_{P_4} \cdot p_{O_2} \left(1 + \frac{p_x}{p_{P_4} + p_{O_2}}\right) d^2 \quad (35)$$

where K' is a constant. But it has been shown that if the intensity of the light is kept constant then the rate of reaction is given by

$$-\frac{dp_{O_2}}{dt} = p_{O_2}^2 \cdot p_{P_4} \times \text{constant} \quad (36)$$

so that the value of $f(p_{O_2}, p_{P_4})$ must be independent of the concentration of phosphorus vapour. The rate of reaction will now be given by

$$-\frac{dp_{O_2}}{dt} = K'' p_{O_2}^2 \cdot p_{P_4} \left(1 + \frac{p_x}{p_{P_4} + p_{O_2}}\right) d^2 \quad (37)$$

But if p_{P_4} and d are maintained at constant values (37) can be simplified to

$$-\frac{dp_{O_2}}{dt} = K p_{O_2}^2 \left(1 + \frac{p_x}{p_{P_4} + p_{O_2}}\right) \quad (38)$$

Rearranging and integrating

$$-Kt = \int \frac{dp_{O_2}}{p_{O_2}^2 \left(1 + \frac{p_x}{p_{P_4} + p_{O_2}}\right)} \quad (39)$$

The expression under the integral sign may be rearranged to a more suitable form for integration as is shown in

detail below.

Let $y = \frac{p_{O_2}}{p_{P_4}}$; $a = p_{P_4}$; $c = 1 + \frac{p_x}{p_{P_4}}$;
then

$$\int \frac{dp_{O_2}}{p_{O_2}^2 \left(1 + \frac{p_x}{p_{P_4} + p_{O_2}}\right)} = \frac{1}{a} \int \frac{(1+y)}{y^2(y+c)} dy$$

$$= \frac{1}{ac} \int \left(\frac{1}{y^2} + (1-c) \left(\frac{1}{y} - \frac{1}{y+c} \right) \right) dy = \frac{1}{ac} \left\{ -\frac{1}{y} + (1-c) \log \frac{y}{y+c} \right\} + \text{constant}$$

Now introducing the values for a, y and c the expression becomes

$$-Kt = \frac{1}{p_{P_4} + p_x} \left(-\frac{p_{P_4}}{p_{O_2}} + \frac{p_x}{p_{P_4} + p_x} \cdot \log \frac{p_{O_2}}{p_{O_2} + p_{P_4} + p_x} \right) + \text{const.} \quad (40)$$

There is a further complication to be disposed of in that p_x must be multiplied by the appropriate inert gas factor μ , 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, the velocity constant K is given by,

$$K = \frac{1}{t} \cdot \frac{1}{p_{P_4} + \mu p_x} \cdot \left[\frac{p_{P_4}}{p_{O_2}} - \frac{p_{P_4}}{p'_{O_2}} + \log \left(\frac{p'_{O_2}}{p_{O_2}} \cdot \frac{p_{O_2} + p_{P_4} + \mu p_x}{p'_{O_2} + p_{P_4} + \mu p_x} \right) \right] \frac{\mu p_x}{p_{P_4} + \mu p_x} \quad (41)$$

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

A series of experiments in which different pressures of inert gases and varying lengths of illumination were used, was carried out. The inert gases used were

argon and nitrogen. In Tables 19 and 20 are shown typical sets of results obtained from these experiments. The results are also shown graphically in Figs. 10 and 11 where

$$Z = \frac{1}{p_{p_4} + \mu p_x} \left[\frac{p_{p_4}}{p_{o_2}} - \frac{p_{p_4}}{p_{o_2}'} + \log \left(\frac{p_{o_2}'}{p_{o_2}} \cdot \frac{p_{o_2} + p_{p_4} + \mu p_x}{p_{o_2}' + p_{p_4} + \mu p_x} \right)^{\frac{\mu p_x}{\mu p_x + p_{p_4}}} \right]$$

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.

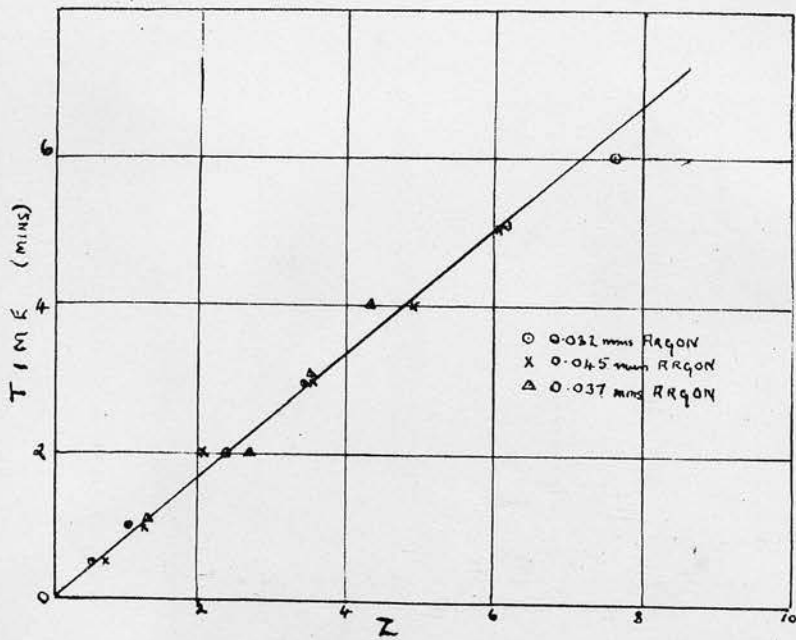


Fig. 10.

Table No 19

Argon.

$$Z = \frac{1}{p_{p_4} + \mu p_x} \left[\frac{p_{p_4}}{p_{o_2}} - \frac{p_{p_4}}{p'_{o_2}} + \log \left(\frac{p'_{o_2} \cdot p_{o_2} + p_{p_4} + \mu p_x}{p_{o_2} \cdot p'_{o_2} + p_{p_4} + \mu p_x} \right)^{\frac{\mu p_x}{p_{p_4} + \mu p_x}} \right]$$

pressure of Argon (mm Hg)	Initial Conc of Oxygen (seconds)	Amount of Oxygen used up (seconds)	$\frac{\text{Initial Conc } O_2}{\text{Final Conc } O_2}$	Z	Length of illumination t (mm)
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	1.27	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

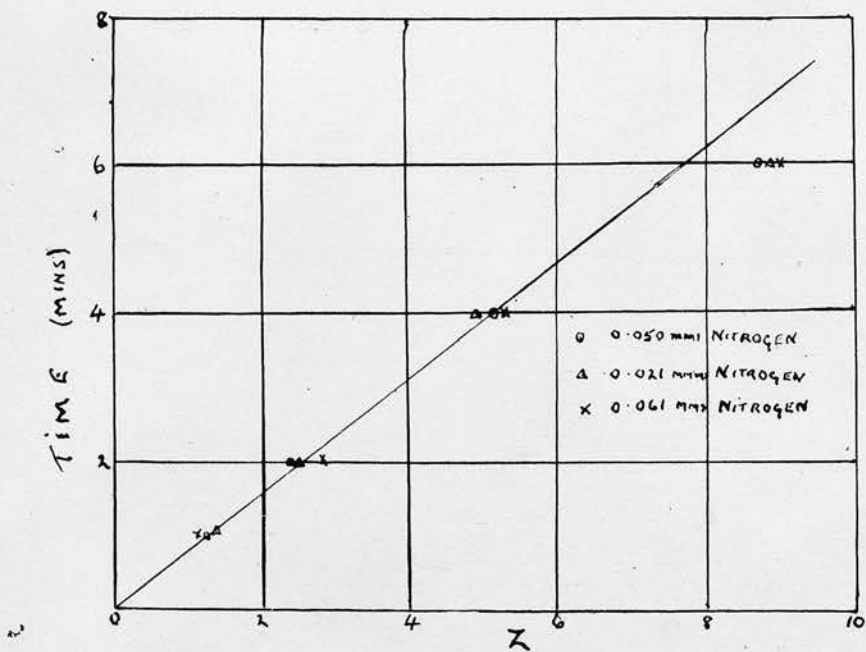


Fig. 11.

Table No 20

Nitrogen

$$Z = \frac{1}{p_{p_4} + \mu p_x} \left[\frac{p_{p_4}}{p_{o_2}} - \frac{p'_{p_4}}{p'_{o_2}} + \log \left(\frac{p'_{o_2}}{p_{o_2}} \cdot \frac{p_{o_2} + p_{p_4} + \mu p_x}{p_{o_2} + p'_{p_4} + \mu p_x} \right) \frac{\mu p_x}{p'_{p_4} + \mu p_x} \right]$$

pressure of Nitrogen (mm Hg)	Initial Conc of Oxygen (seconds)	Amt of Oxygen used up (seconds)	Initial Conc O ₂ / Final Conc O ₂	Z	Length of illumination 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

The transformation of white to red phosphorus by means of ultraviolet light.

During the course of experiments on the initiation of chains by ultraviolet light in the phosphorus-oxygen reaction, it was observed that frequently the surface of the reaction bulb became covered with what seemed to be a deposit of red phosphorus. It could be removed by heating, when inflammation took place and by addition of bromine water. Apparently the ultraviolet light, besides catalysing the oxidation reaction could also in some way transform white phosphorus to red phosphorus.

When phosphorus vapour and oxygen are allowed to combine at slightly higher pressures than those used for the study of the stable reaction, however, no red phosphorus can be observed on the walls of the reaction vessel. Now since it has been shown by various authors that the conversion of white to red phosphorus takes place through an intermediate stage i.e. through the formation of P_2 molecules, it was suggested that the initiation of the chains by ultraviolet light depends primarily on this dissociation of P_4 molecules into P_2 molecules. It has not however been definitely shown that the absorption of light by P_4 molecules results in the formation of red phosphorus. Although it seems unlikely, it was 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 to 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 the quantum yield is one. In the following experiments an attempt was made to observe and measure the transformation of white to red phosphorus and to obtain the value of the ratio

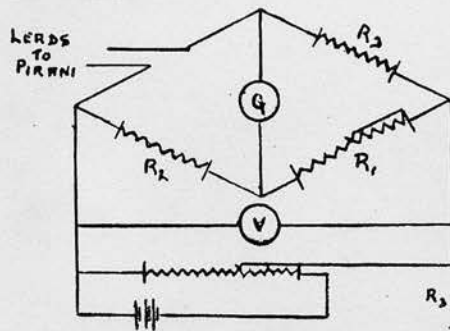
$$\frac{\text{rate of oxidation of P}_4}{\text{rate of clean up of P}_4} .$$

EXPERIMENTAL.

The apparatus was similar to that used in previous experiments apart from the fact that pressures, and pressure changes were measured by means of a Pirani gauge.

The circuit for this is shown in Fig.12. The Pirani gauge had a platinum filament 0.01 mms. in diameter and was kept at about 100°C. At this temperature the filament was not attacked by the phosphorus vapour. The principle of the method employed was quite simple. It consisted in admitting phosphorus vapour to the reaction vessel, illuminating the vessel with light from a mercury arc and following the change in pressure i.e. the clean up of phosphorus vapour by the Pirani gauge. The method of measuring pressures and pressure changes was as follows: -

With the apparatus pumped out, the voltage across the bridge was adjusted so that no deflection of the galvanometer took place on depressing the tapping key.



R_3, R_2 - FIXED RESISTANCES
 R_1 - VARIABLE RESISTANCE

CIRCUIT FOR PIRANI GAUGE

Fig 12.

This gave the zero reading corresponding to a voltage V_0 . Phosphorus vapour was allowed to enter the reaction vessel up to the desired pressure, and the bridge balanced up again. This gave a higher voltage V_{p_4} because of the conductance of heat from the filament by the molecules of vapour. After this initial reading the rheostat was adjusted so that the value of V_{p_4} was slightly low. This reading was noted. The reaction vessel was then illuminated, and the time required for the galvanometer indicator to reach the position of zero deflection taken. This procedure was repeated until the change in pressure was too small to measure.

Now if p is the pressure of vapour corresponding to V_{p_4} then

$$\frac{V_{p_4}^2 - V_0^2}{V_0^2} = kp$$

where k is a constant depending on the nature of the gas present. The absolute pressures of oxygen and phosphorus vapour were obtained by calibrating the Pirani gauge. The calibration of the gauge for phosphorus vapour was carried out by observing the values of $(V_{p_4}^2 - V_0^2)$ for different pressures of phosphorus vapour in the reaction vessel. The pressure of phosphorus was regulated by immersing the phosphorus reservoir in baths at different temperatures. The pressures corresponding to these being obtained from International Critical Tables and are extrapolated from measured

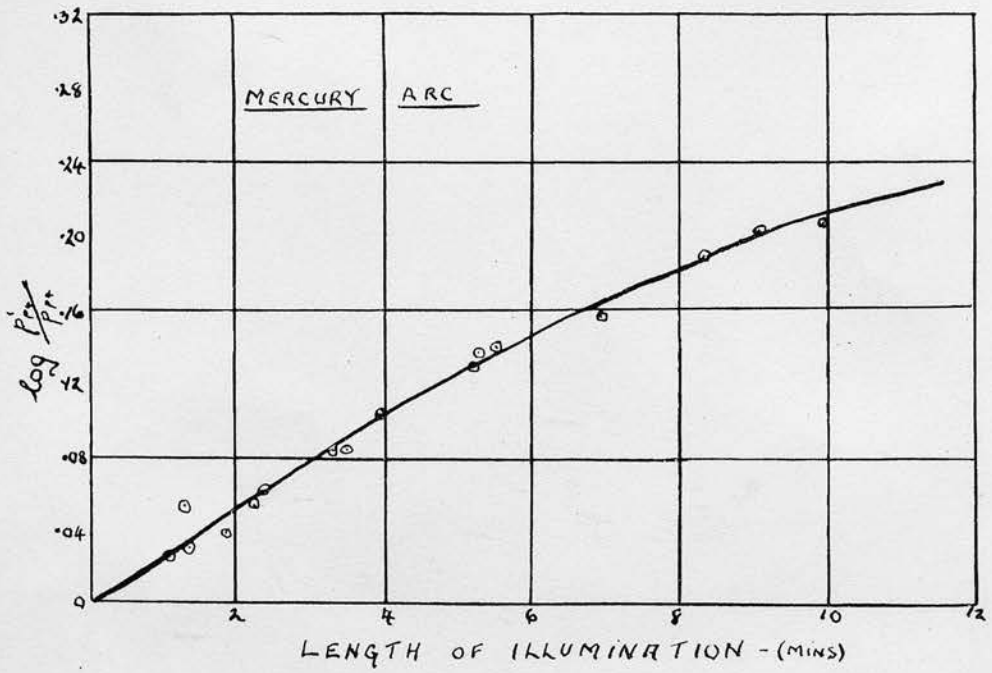


Fig. 13.

pressures at higher temperatures. Calibration of the gauge for oxygen was carried out by reading simultaneously the pressures on the McLeod gauge and the Pirani gauge. Changes in $V_{p+}^2 - V_0^2$ were sufficient however to determine the rates of reaction.

RESULTS.

A few typical runs 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. 13 that this deposition seems to occur approximately according to a unimolecular equation. As the rate of reaction was very small the Pirani gauge readings were not converted to pressures in mms. of mercury. Table (21).

Table No 21

Pressure of phosphorus vapour = 0.015 mm. Hg.

Pressure of Phosphorus vapour $V_{P_4}^2 - V_0^2$	Log $\frac{P_0}{P}$	Length of Illumination (mins.)	t (mins) $\log \frac{P_0}{P} = 0.15$
1929	-	-	-
1708	0.053	1.3	
1523	0.103	4.0	
1408	0.137	5.2	6.2
1213	0.202	9.1	
1008	0.282	12.3	
1634	-	-	-
1498	0.037	1.9	
1359	0.080	3.5	
1068	0.185	8.4	6.7
727	0.352	19.3	
2506	-	-	
2311	0.035	1.4	
2168	0.063	2.4	
1960	0.107	5.9	6.9
1760	0.153	7.0	
2052	-	-	
1924	0.028	1.1	
1820	0.052	2.3	
1707	0.080	3.3	6.7
1487	0.140	5.6	
1275	0.207	10.0	

The following table gives results obtained from a series of experiments in which an inert gas argon was added to the phosphorus vapour and the rate of clean up of the phosphorus vapour measured. The pressure of phosphorus vapour and the intensity of illumination were kept constant whilst the pressure of inert gas was altered.

Table No 22Argon Pressure of phosphorus vapour = 0.015 mm. Hg.

Pressure of Inert Gas (mms. Hg)	Log $\frac{P_0}{P}$	Length of Illumination T (mins.)	$\frac{\log \frac{P_0}{P}}{T}$	t (mins.)
0.00	0.040	4.0	0.010	
0.00	0.068	7.3	0.009	
0.00	0.091	10.0	0.009	
-	-	-	-	13.1
0.014	0.055	6.1	0.009	
0.014	0.085	9.1	0.009	
-	-	-	-	13.1
0.031	0.037	3.6	0.010	
0.031	0.084	8.5	0.010	
0.031	0.118	13.0	0.009	
0.031	0.146	16.6	0.008	
-	-	-	-	12.9
0.046	0.041	6.8	0.006	
0.046	0.094	15.0	0.006	
-	-	-	-	19.3
0.070	0.041	9.4	0.004	
0.070	0.095	22.7	0.004	
-	-	-	-	28.5
0.00	0.051	5.0	0.010	
0.00	0.073	8.1	0.009	
0.00	0.109	10.5	0.010	
				12.8

It is seen that the addition of an inert gas does alter the rate of transformation of white phosphorus to red, until a considerable pressure of the inert gas is present. At these pressures the rate of the transformation is considerably decreased. It may be concluded therefore that illumination of P_4 molecules by ultraviolet light, causes a dissociation of the P_4 mol-

ecules 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. But 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 result in the formation of red phosphorus the remainder being reflected from the surface. Thus if the surface of the walls of the reaction vessel acts as a fairly efficient reflector of P_2 molecules, then no decrease in the rate of transformation of white to 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 22. 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 ultraviolet light, so that by comparison with the rate of clean up of phosphorus vapour under exactly similar conditions, some idea of the lengths of the chains initiated in the stable oxidation could be obtained. The method employed was as follows:-

By adjusting the voltage across the bridge V_0 was found as before. Phosphorus vapour was admitted to the desired pressure and the corresponding reading of the Pirani gauge noted. Oxygen was allowed to enter the reaction vessel through a previously calibrated capillary, until the required pressure was reached, when illumination commenced. After illumination had ceased, the phosphorus vapour was condensed out by means of liquid air, the pressure of oxygen measured by taking the corresponding Pirani reading. The oxygen was then pumped off, and the phosphorus allowed to warm up, (by placing it in a thermostat) until the original pressure was reached, and the Pirani reading taken. In this way it was hoped that changes in pressure of both the oxygen and the phosphorus vapour might be followed. However although the oxygen pressure change could be measured in this way no change in the phosphorus pressure was observed - the pressure readings being rather erratic. This probably was due to one or a combination of the following three factors:-

(i) that the change in phosphorus vapour was too small to measure. This seems to be very unlikely in view of the measurements made in the clean up.

(ii) 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 result of the combination of the oxygen with the phosphorus did not result in its complete oxidation to P_2O_5 . In that case some lower oxide with a measurable vapour pressure would be formed. Hence final measurements of the phosphorus pressure would include the pressure of this lower oxide, and would be inaccurate.

S U M M A R Y.

The effect of the foreign gases Hydrogen, Helium and Deuterium on the lower explosion limit of P_4-O_2 mixtures has been studied, and the values for the inert gas effect determined in each case. Comparison of these values showed conclusively that hydrogen has a greater inert gas effect than is predicted by theory. A partial explanation of this may lie in the assumptions made as to the nature and physical constants of the chain carriers.

The absorption spectrum of phosphorus vapour was obtained for different pressures of phosphorus vapour. Definite absorption was seen to take place in the region of and below the mercury line at $2537A^\circ$.

Illumination of P_4-O_2 mixtures at pressures below the lower explosion limit produced two effects, viz.

- (a) a displacement of the lower limit towards smaller pressures
- (b) a reaction between the P_4 and O_2 molecules below the lower limit.

Further experimental work was carried out on the displacement of the lower limit in order to test the statement that the explosion limits in a chain reaction are independent of the rate of initiation of the chains.

During this work it was shown that the displacement is not permanent but slowly decays on allowing the reaction mixtures to stand before proceeding to explosion. A period of five to six minutes is necessary before normal conditions are regained. Illumination of P_4 vapour alone resulted in a displacement of the lower limit of only half the value of that obtained when oxygen was present, although the slopes of the corresponding decay curves were similar. Moreover the displacement was the same for different pressures of oxygen, although it was obviously effected by a change in the condition of the walls.

All the evidence obtained which was based on the transfer experiments, showed that the displacement of the lower limit was a wall effect and was not due to the production of active centres in the gas. This wall effect was due in the first case to the formation of P_2 molecules from the P_4 molecules.

Illumination of phosphorus-oxygen mixtures above the upper explosion limit resulted in a displacement of this limit towards higher pressures. It was suggested that the explosion limit found under normal conditions is low owing to the fact that the rate of starting of the chains is too slow for the relationship predicted by chain theory to hold.

The stable reaction between P_4-O_2 molecules init-

iated by the ultraviolet light was shown to be a chain reaction, the kinetics of which was studied and the rate of reaction was found to be given by

$$R = - \frac{d[O_2]}{dt} = [P_4][O_2]^2 \times I \times \text{constant.}$$

The effect of inert gases on the reaction rate was studied and it was shown that the velocity constant was independent of the concentration of inert gas present.

Phosphorus vapour on exposure to ultraviolet light was shown to be converted into red phosphorus. The rate of transformation was measured and the reaction found to be approximately unimolecular.

In conclusion the author wishes to express his gratitude to Dr E. B. Ludlam for his continued interest and advice during this work, and also to the Trustees of the Moray Fund of Edinburgh University for grants towards the cost of apparatus.

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