
Kinetics of the oxidation of phosphorus

Roxsburgh, Henry Lindsay

PhD

1934

CONTENTS.

Part I.

Part II.

The fundamental idea which became the basis on which the present theory of chain reactions was raised, was the suggestion by Einstein,[1.] that, in a photochemical reaction, there should be some simple relation between the number of quanta absorbed and the number of molecules which undergo reaction. Such a relationship was found by Warburg[2.] in a series of researches from 1912 to 1921; he proved that in the photochemical decomposition of hydrogen bromide and iodide, the quantum yield is two. It was shown, however, by Bodenstein in 1913 that in the photosynthesis of HCl, the number of molecules of HCl formed was enormously greater than the number of quanta absorbed. This led Nernst[3.] to suggest the following scheme, which satisfactorily explained the anomaly. In this "Nernst chain" it was postulated that a chlorine molecule absorbed a quantum of light and was split up into two chlorine atoms. These atoms then reacted with Hydrogen molecules to form hydrogen chloride and hydrogen atoms. The latter in their turn attacked more chlorine molecules giving more HCl and liberating chlorine atoms, and so set up chains in the gas mixture. Thus:-

$Cl_2 + hv \rightarrow 2Cl$

$Cl + H_2 \rightarrow HCl + H$

$H + Cl_2 \rightarrow HCl + Cl$

$Cl + H_2 \rightarrow HCl + H$ and so on.

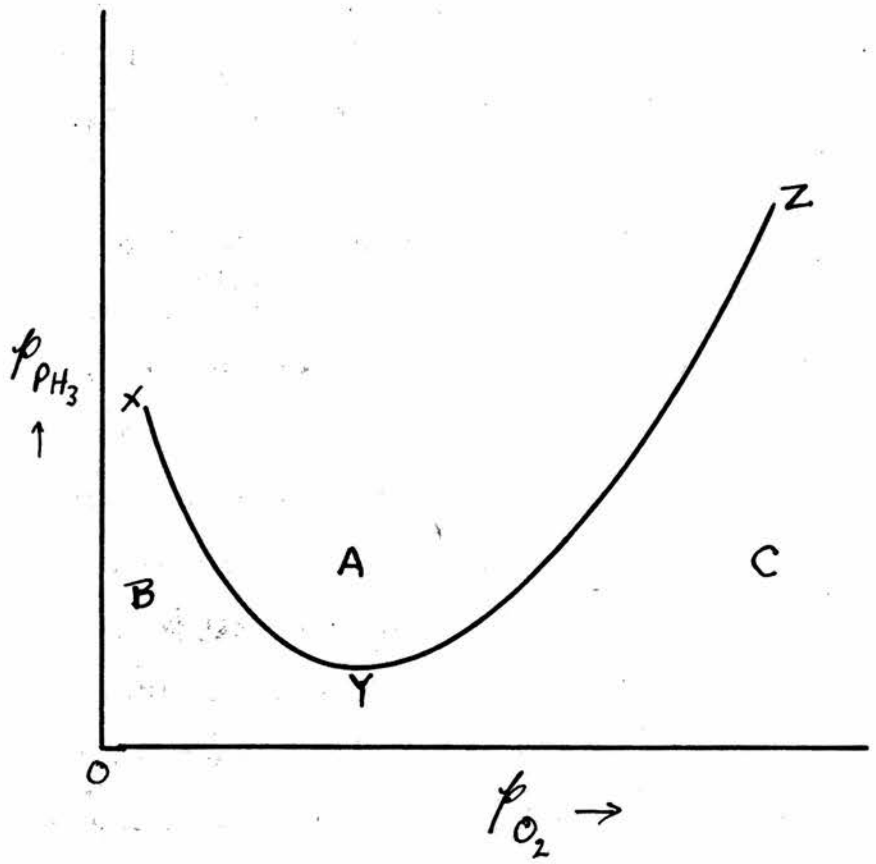
As the reaction $H_2 + Cl_2 \rightarrow 2HCl$ is exothermic, it is quite possible for many molecules to react following absorption of one quantum. The number of links in the chain is only limited by the possibility of recombination of the chlorine atoms and the hydrogen atoms, either at the walls of the containing vessel or in collisions with foreign gases when such are present. (It is not possible that the hydrogen and chlorine atoms could recombine without some third body to absorb the energy liberated in the reactions -

$$H + H \rightarrow H_2$$

and $$Cl + Cl \rightarrow Cl_2$$)

The number of links in each chain, i.e. the number of molecules of hydrogen chloride formed per Cl atom produced by light is called the "chain length." Whether such a scheme could be applied to purely thermal reactions was another matter, for at this time the only criterion of the chain character of a reaction was the high quantum yield.

Another factor in the rapid development of the theory of chain reactions was due to the study of unimolecular reactions, and the controversy over the origin of the energy of activation in unimolecular gaseous reactions.[4.] In order to react, molecules must be activated in some way. Thermally this must occur during collisions between molecules. In this case, the rate of activation should be proportional to the square of the concentration; i.e. the reaction would be bimolecular. In genuine unimolecular re-


p_{PH_3} ↑
X
Y
Z
A
B
C
O
p_{O_2} →

actions, it is at first sight difficult to understand how activation involves collisions between molecules. The solution of the problem was first attempted by Christianson and Kramers,[5] who showed how a reaction may exhibit unimolecular characteristics in spite of the activation occurring in two body collisions. The essence of their argument was that activated product molecules may transfer energy to unactivated reactants by collision.

It is well known that for certain reactions, such as oxidation of phosphorus and phosphine, there are certain pressures of oxygen for a given phosphine pressure, between which the reaction goes very quickly, and outside which there is no appreciable reaction. The position may be better explained by means of a diagram. In the case of mixtures represented by points in the area A, explosion takes place spontaneously as soon as the gasses are mixed, wheras in the areas representing higher and lower oxygen pressures, C and B respectively, there is no reaction. The line XY represents the lower explosive limit and YZ the upper limit. The position of XY is dependent on the diameter (d) of the tube, and on the presence of inert gases (X). Over a limited range XY may be represented by the equation:-

$$p_{PH_3} \times p_{O_2}\left(1 + \frac{\mu p_X}{p_{PH_3} + p_{O_2}}\right) d^2 = \text{const.} \qquad 6.$$

This "constant" is almost independent of temperature. The position of the upper limit YZ depends on the presence of foreign gases, (in this case the presence of foreign gases decreases the tendency to explode, wheras at the lower limit the inert gas facilitates explosion) but not at all on the diameter of the reaction tube. The equation for the explosive limit ZY has been found to be:-[7.]

$$[PH_3] = \frac{k_1[O_2]^2 + k_2[O_2][X]}{1 - k_3[O_2]} \qquad \text{(Dalton)}$$

To explain these explosive limits it was suggested by Semenoff[8.] that the reactions under consideration were chain reactions, just as the photosynthesis of ACl is a chain reaction, but that initiation of the chains was brought about by a thermal process instead of photochemically, and that the lower and upper limits were at that point where "branching" of the chains just balanced the deactivation by the walls of the vessel and by the gas.

Until 1928 it was thought initiation of chain reactions occurred homogeneously, either thermally or photochemically. About this time it was suggested that some activated molecule or atom could be formed on a surface and then leave the surface with sufficient energy to start a reaction in the gas. For instance, in 1928, Garner and Gomm, while working on the reaction between CO and O_2, obtained results which led them to suggest that a chain reaction could be started at a surface. Bodenstein[10.] had found the CO-O_2 reaction to be heterogeneous, but Garner and Gomm found that up to 580°C (and above for pressures less than 0·3 cm) the reaction is heterogeneous, but that when the rate of surface interaction exceeds a certain amount, a flame is generated in the gas mixture. The surface reaction does not appear to influence the explosion phenomena beyond supplying sufficient energy to <u>start</u> the homogeneous reaction: as long as the minimum energy is available and the pressure is above the critical value the flame makes its appearance. The supply of larger amounts of energy by the surface reaction does not appreciably alter the pressure at which ignition will occur at any temperature. This constancy of ignition pressure led Garner and Gomm to suggest that a chain mechanism was responsible for the explosion, and that the chain reaction taking place just before explosion might be of a different character from that in the flame itself.

Lewis and Feitknecht[11.] bring evidence to show that the bromine sensitised decomposition of ozone is a reaction that starts on the walls and is then propagated through the gas. It is suggested that Br_3O_8 is formed at these temperatures, while at higher temperatures it tends to decompose and liberates molecules or atoms into the gas space, which are capable of starting chains. The evidence here for surface initiation is however rather scanty.

In the case of the decomposition of ClO_2 it has been found[12.] that while the rate of reaction varies as $(ClO_2)^{\frac{1}{2}}$, it also varies directly with the total gas pressure, a fact which suggests the presence of a chain reaction. They also found that by treating the walls of the vessel it was possible to keep ClO_2 without any reaction for a certain time, at the end of which explosion occurred. From this fact they concluded that the wall was the origin of the reaction, as otherwise some reaction would have been observed during the induction period. While not unreasonable, the explanation is not the only possible one, for it is known from packing experiments that the walls are responsible for destruction of chains.

Rather more important experiments from the point of view of surface starting of chains are those of Alyea and Haber[13.] and Alyea,[14.] in which crossed streams of hydrogen and oxygen were employed. Streams of hydrogen and oxygen were made to cross each other in an atmosphere, and under suitable conditions no explosion or inflammation took place. On introducing a quartz rod into the meeting point of the streams, the gas exploded and the flame persisted until the rod was withdrawn. The quartz rod was at a temperature <u>below</u> that of the mixed gases so there could be heating effect to cause the explosion. Rods of glass, porcelain, copper or iron initiated explosion just as did quartz, but aluminium was ineffective. This may be due to a film of oxide on the aluminium. Alyea has explained the explosions as being due to an adsorbed layer of hydrogen atoms on the surface of the rod. Atoms then leave this layer and initiate reaction chains which extend out into the gas phase. The ineffectiveness of aluminium in bringing about explosion might then be explained by the fact that alumina is quite inert in bringing about the recombination of hydrogen atoms,[15] and should be equally inert in the activation of hydrogen molecules. The view that hydrogen atoms start the chains is supported by the suggestion[16.] that hydrogen atoms, formed in the photochemical decomposition of ammonia, start chains in hydrogen oxygen mixtures. This evidence, however, is not conclusive, as Taylor and Salley[17.] show that the NH_2 group and intermediate oxidation products help to propagate the chains, but Haber and Oppenheimer,[18.] on mixing with oxygen a stream of hydrogen that had passed over a hot tungsten wire, and therefore contained some atomic hydrogen, observed inflammation at temperatures lower than the explosive limit. Similar results were obtained by Semenoff, Nalbandjan, and Dubowizky,[19.] using a discharge tube instead of a tungsten wire to produce the atomic hydrogen, and they also found the position of the limit to be changed. Earlier experiments by Mitchell and Marshall[20.] showed that "active" hydrogen, i.e., hydrogen which would reduce cupric oxide at lower temperatures than would ordinary hydrogen molecules, was formed when hydrogen containing small amounts of oxygen was led over a platinum catalyst. It was suggested at the time that this active hydrogen was H_3,[21.] but later work has shown it to be atomic hydrogen.

Taylor[22.] has suggested that atomic hydrogen may be formed at a surface in the following way. Assume the oxygen to be adsorbed on the surface in the atomic form S(O). Then there are two reactions capable of liberating atomic hydrogen.

$$(1) \quad S(O) + H_2 \rightarrow S(OH) + H\nearrow$$

$$(2) \quad S(OH) + H_2 \rightarrow S(OH) + H\nearrow$$

Disregarding the heats of adsorption it is known that both these reactions are exothermic in the gas phase[23.] and thus provide a possible means for the release of Hydrogen atoms.

Further use of the method of crossed streams was made by Thompson[24.] in investigating the carbon disulphide oxygen reaction, and it was found that surfaces aided the explosion as in the hydrogen oxygen reaction.

The position regarding the surface starting of chain reactions has been summarised by Hinshelwood.[25.]

More recent experiments are those of Melville and Ludlam,[26.] in which the reaction between oxygen and phosphorus vapour is initiated at a surface. The effect of hot metal filaments of Pt. Au. Ag. W and Mo on the reaction were investigated. It was found that using a Pt filament the reaction takes place wholly on the surface of the filament, but that with a tungsten filament it was possible to start a reaction in the gas phase. It is probable then for some reactive substance to be formed on the surface of the filament, which then leaves the surface and starts reaction in the homogeneous phase. The effect of the inert gases neon and argon was found and it was seen that the reaction was accelerated in presence of these gases. The neon had a smaller accelerated effect than the argon, as is to be expected owing to its smaller atomic diameter and mass. The results were worked out and were found to agree with a theory based on Semenoff's expression:-[27.]

$$\text{chain length} \propto p_P \times p_{O_2} \left(1 + \frac{\mu p_X}{p_P \times p_{O_2}}\right) d^2$$

(μ = constant dependency on nature of inert gas.) This shows conclusively that the reaction takes place not wholly on the surface but is predominantly a gas phase reaction. These results and those of Alyea and Haber show quite definitely that, given suitable conditions, it is possible to start a chain reaction at a surface. Further experiments using filaments were done by Ritchie,[28.] and Ritchie, Brown and Muir.[29.] It was found that a chain reaction between sulphur and oxygen could be started on the surface of a filament of metal and pyrex glass. Under suitable conditions a glow throughout the reaction vessel was obtained on switching on the filament, and inert gas effects compatible with the reaction being a chain reaction were obtained.

It is necessary at this stage to make some distinction between two possible types of chain initiation at surfaces.

(1). Initiation by a purely chemical reaction - an atom or radicle on leaving the surface can, by virtue of some chemical property, react with other molecules in the gas and start chains. Such a reaction is that between phosphorus and oxygen, where it has been suggested that the gas reaction can be caused by hydrogen atoms leaving the surface.

(2). Reaction started by atoms or molecules leaving the surface which, by virtue of their energy, can dissociate or activate molecules in the gas so that a chain reaction results. It was suggested by Garner and Gomm[9.] that this kind of reaction might occur in the case of carbon monoxide and oxygen.

Thus, in order to study a chain reaction, there are three stages to be considered:-

(a) Initiation of the chain.

(b) Propagation of the chain carriers through the gas phase.

(c) Destruction of the chain carriers.

Now if the chains are started by thermal means in the gas phase, it is not possible to separate experimentally (a) from (b) and (c). If, on the other hand, chain centres can be formed on a surface, say a hot filament, and shot out into the gas phase, it is possible to alter the conditions of formation of the centres without affecting materially the propagation and destruction of them. It has, in fact, been shown that a hot tungsten, molybdenum or glass filament can be used to initiate a stable chain reaction between phosphorus and oxygen.[30.] Experiments have also shown that the oxidation of PH_3

is a similar reaction to the oxidation of phosphorus itself[31] - a stable chain reaction can be started by means of a mercury arc (photo-sensitised reaction) or a zinc spark (direct reaction). Thus with suitable means of formation of chain carriers, phosphine oxygen mixtures below the explosion limit are capable of propagating stable chains. It is then reasonable to expect that a hot surface, such as a filament, could be used to investigate the mechanism of the phosphine oxygen reaction.

Apart from qualitative demomstration of such heterogeneous initiation, the method may be employed to elucidate several points in the theory of chain reactions. Before these are enumerated and their importance emphasized it will be desirable to give a detailed account of the quantitative theory of the oxidation of phosphine, both at the explosive limits and also outside the limits.

Suppose that there are two chain carriers Xo and Xp and that these react thus:-

$Xo + PH_3 = Xp$.......... veloc. coefft. = k_3

$Xp + O_2 = Xo$ ....etc. " " = k_2

Let the rate of production of Xo (from the source of the reaction and not from destruction of Xp) be F(c), i.e. a function of the concentration of the reactants. The fact that the walls of the vessel inhibit the explosion, clearly shows that the chain carriers are destroyed there. The rate of this process is K Xo and K Xp , where K is the rate that and K Xp , where K is the rate that Xo, Xp diffuse through the gas mixture to the walls. These assumptions alone do not admit of the possibility of explosion. It was Semenoff[8] who realised that it was necessary to assume that in some collisions two chain carriers emerge from the colliding bodies, in other words, the <u>chain branches</u>. Further, suppose that branching occurs in Xp - O_2 collisions and that the probability of branching in such an effective collision is (α -1); i.e. α is the mean number of Xo formed in an effective Xp - O_2 collision. The stationary concentration of Xo and Xp may now be written down and can be given in the equations:-

$$\frac{d[X_o]}{dt} = F(c) + \alpha k_2 [X_p][O_2] - k_3 [X_o][PH_3] - K[X_o] = 0$$

$$\frac{d[X_p]}{dt} = k_3 [X_o][PH_3] - k_2 [X_p][O_2] - K[X_p] = 0$$

Solving for $[X_p]$ & $[X_o]$

$$[X_o] = \frac{k_2 [O_2] F(c) + K F(c)}{(1-\alpha) k_2 k_3 [PH_3][O_2] + k_2 K[O_2] + k_3 K[PH_3] + K^2}$$

This may be simplified in two ways: K^2 can be neglected, for, $k_1 [O_2]$ or $k_2 [PH_3]$ are large compared with K if the chains are long; also k_2 can be put equal to k_3. Exact experimental data in support of these simplifications are given in experiments on the photochemical oxidation of phosphine[31,32], in which it is shown that (a) a considerable distance below the lower limit (1mm. total pressure) the chain length is about 10^2; (b) nearly every collision in the above reaction is an effective one.

In order that the reaction may be explosive, the denominator of the above expression must approach zero, and it will be observed from the above theory that this possibility is purely dependent on the negative value of the first term of the denominator. As the pressure of a phosphine-oxygen mixture is raised the first term will increase more rapidly than the other two, and thus the value of the denominator will approach zero and explosion occur. At the limit then:-

$$(\alpha - 1)\, k_2 [PH_3][O_2] = K \left\{ [O_2] + [PH_3] \right\}$$

In the explosive region the denominator (equation 1) will be negative, but as an upper limit exists, some other additional factor which is unimportant at low pressures makes an appearance whereby the value of Xo is brought back to a finite quantity. The exact form of this factor is not known.

Outside the limits, at room temperature, F(e) is so small that there is no measurable reaction. If, however, the rate of starting be sufficiently increased, then it should be possible to observe and investigate the kinetics of a stable reaction outside the limits. This possibility has been realised in the photo-oxidation of phosphine below the lower limit,[31,32] and the kinetics of the stable and explosive reactions have been shown to bear a very exact interrelationship.

The main problems requiring elucidation are these:-

1. The form of the inhibition factor causing the

appearance of the upperllimit. The relationship of the kinetics of the stable and unstable reactions above and at the upper limit.

2. The nature of the transition from the stable reaction below the lower limit to that above the upper limit.

3. The mechanism of the surface reaction leading to the ejection of a chain carrier.

4. Displacement of limit by alteration of rate of initiation of chains.

(It will be observed from the above equation for the limit that the factor F(c) has completely disappeared. That is, the <u>limit</u> should be <u>independent</u> of the number of <u>chains starting</u>. If this is really the case then neither limit should be altered if the rate of initiation is artifacially changed; e.g. by presence of a hot filament.

First of all a detailed study has been made of the thermal decomposition of phosphine on tungsten and molybdenum; this is followed by an investigation of the mechanism of the oxidation. Unfortunately only small amounts of oxidation reaction proved to be homogeneous. In consequence the problems tabulated above cannot be solved by the filament method. In the second part of this thesis photochemical methods have been used to provide the data lacking owing to the oxidation taking place almost exclusively on the surface of the filament.

EXPERIMENTAL.

Preparation of Gases.

(a) Phosphine was prepared by dropping potassium hydroxide on phosphonium iodide. The impure phosphine evolved was then passed over sodium hydroxide, calcium chloride, and finally phosphorus pentoxide, collected in a liquid air trap, and then fractionally distilled three times, the first and last quarters being rejected in each distillation.

(b) Hydrogen, oxygen, argon, nitrogen and ammonia came from cylinders and were purified by the following methods:-

(1) Hydrogen. Passed over Pt Asbestos and then P_2O_5 to remove oxygen as water.

(2) Oxygen. The cylinder oxygen was 99½% pure, and the only treatment was passage over phosphorus pentoxide to remove moisture.

(3) The "inert gases", argon and nitrogen were first of all passed over a hot tungsten filament to remove oxygen, and then over phosphorus pentoxide.

(4) Ammonia. Purified by fractional distillation over liquid air, after passage over soda-lime.

Apparatus.

The essential parts of the apparatus were made of soft glass tubing and are shown diagrammatically in Fig. 1. The reaction tube (K) was 3cm. in diameter and about 20cm. long. This was surrounded by a water bath kept at a constant temperature, usually 20°C.

The reaction tube was evacuated by a three stage mercury condensation pump, backed by a "Hyvac" oil pump. With this arrangement a pressure of less than 10^{-5} mm. of mercury could easily be attained. In addition to gas reservoirs and pipettes, suitable side tubes which could be cooled in liquid air were connected to the apparatus in order to facilitate the analysis of gas mixtures containing phosphine. A small Töpler pump (B) was used for transferring gas in the reaction tube to a tube containing a platinum wire for analysing hydrogen oxygen mixtures obtained in the oxidation experiments.

Several types of pressure guage were used. M_2, M_3 & M_4 were capillary mercury manometers which were used for measuring pressures above 30mm. For the lowest pressures the McLeod guage (Mc) was convenient, and as the volume of the bulb was known (200cc.) it could be used to find the volume of any other section of the apparatus. For higher pressures a glass spring manometer was used. Later experiments were made with an oil manometer (M). The right limb of this manometer was of much wider tubing (2·5cm.) than the left limb (0·4cm.), so the movement of the oil in the left limb for a given pressure change was nearly double that in a manometer with limbs of equal bore. Apiezon oil "B" (Shell-Mex and B.P.) of v.p. less than 10^{-7}mm. Hg was used and it did not appreciably dissolve the gases which were used in these experiments.

The oil was thoroughly degassed before using by warming for several hours in a vac. The tap lubricant used was Apiezon grease "L".

The filaments were made of 0·1mm. dia. Tungsten and Molybdenum wire and were for the most part spot welded to 1mm. Nickel leads. In the earliest experiments, attempts were made to pinch the filament in the nickel wire, but this was unsatisfactory as the resistance of the assembly altered and temperatures could not be determined accurately. In this respect the spot welding was quite satisfactory. The nickel leads were in turn spotwelded to borated copper clad wire with which the metal-glass seals were made.

Determination of filament temperature.

In order to eliminate, as far as possible, end losses, the filament was constructed in an unusual manner. Preliminary experiments had shown that the rate of decomposition of the phosphine was conveniently measurable below 600°, so it was not possible to read the temperature of the centre portion of the filament by a micropyrometer and correct for end losses by calculation[33] and so some method depending on the change of filament resistance with temperature had to be used.

The principle of the new method is as follows. Two filaments, one three to four times the length of other, are set up in the reaction tube and run under identical conditions. The reaction velocity due to each filament is determined as well as the hot and cold resistances of the two filaments. The rate of reaction due to the larger filament, less the rate of the small filament, is then the rate due to a central portion of the larger filament, which is at an approximate constant temperature throughout its entire length. Similarly, the difference of resistances of the twoc filaments gives the resistance of this central portion, and from the resistance temperature curve of the metal, the mean temperature of the central portion can be accurately calculated. To ensure that the filaments did run under identical conditions, each formed the arm of a Wheatstone bridge, in which circumstances small losses in the connecting leads were simultaneously balanced out. The electrical connections are shown in fig. 2. F_1 and F_2 denote the large and the small filaments respectively, while R_1 and R_2 are variable resistances, in the form of slidewires, whereby F_1 and F_2 can be balanced out. R_3 is a fixed resistance. R_1, R_2, and R_3 were made of "Constantan" wire of such a diameter as to carry the bridge current (less than 2 amp.) without appreciably changing in resistance. The resistance of each was of the order 1 ohm. R_4 and R_5 were of much higher resistance (ca. 1000 ohms).

Before setting up the bridge it was necessary to find how long the small filament should be in order to eliminate end losses. The choice of dimensions was facilitated by the fact that when PH_3 is decomposed by the filament, a film of red phosphorus appears on the surface of the glass tube containing the filament. Now when decomposition was carried out at low pressures, it was found that the film appeared only on the surface of the glass opposite the central part of the long filament, and that the ends of this film were quite definite. The length of the deposit was taken as a means of finding the effective part of the filament. For a 12cm. filament the film was ca. 9cm. long. The small filament was therefore made 3cm. long.

With F_1 and F_2 in circuit, suitable temperature and pressure ranges were found and the bridge balanced by adjustment of R_5, R_4 being kept constant at 1000w. A run was then made and the rate calculated by the method described below. With the same phosphine pressure another run was carried out, R_1 being substituted for F . R_1, R_2, R_3, R_4, and R_5 are all known, so the resistance of the filaments F_1 and F_2 could easily be calculated. $R_3$was 60cm. of constantan wire, R 1·263 ohms. per cm. As the range of temperatures used in actual experiments was small it was unnecessary to find the reaction velocity due to each filament, at the several temperatures used.

To find the cold resistance of the filaments, a small current, not greater than 0·2 amp. was used, and the reaction tube was filled with gas to prevent the filament heating up. Then R_5 was adjusted so that there was no reading on the galvanometer. The resistances of F_1, F_2 are then found by balancing out the short filaments by R_2 and calculating F_1 by proportion. These values were checked regularly (at least daily).

To adjust the filament at any desired temperature, R_5 is set at a certain value, and the current through the filament altered by the rheostat R_6 until the resistance of the filaments are exactly able to balance the bridge. In order to calculate the filament temperature, the resistance of F_2 for each particular value of R_5 must be known. This is simply done by balancing out F_2 by R_2.

(**Note.** During each experiment, owing to change in pressure in the tube, the rate of loss of heat alters, and so to maintain the balance the current through the filament must be continually adjusted by means of the rheostat R_6).

A specimen calculation follows.

Cold. 20°C. R_2 = 44 cm. wire.
R_5 = 1090 w.
R_4 = 1000 w.
R_3 = 60 cm. wire.

Resistance of long filament leads = $\frac{1040}{1090} \times 1000 \times 1{\cdot}263 \times 10^{-2} = 1{\cdot}21$
" " short " " " $44 \times 1{\cdot}263 \times 10^{-2} = 0{\cdot}56$
" " mid. portion at 20°C = 0·65
" " whole long filt. at 20°C = $0{\cdot}65 \times \frac{4}{3} = 0{\cdot}866$
" " " " " " 0°C = 0·791 (fr. tables)
" " leads = $0{\cdot}56 - 0{\cdot}65 \times \frac{1}{3} = 0{\cdot}34$
" " mid. portion of long filt. at 0°C = $0{\cdot}791 \times \frac{3}{4}$
= 0·593

Calculation of Temperatures - <u>Hot</u>

<u>R_5 set at 440</u>.

R_2 = 41·2 cm. wire.

R_3 = 60 cm. wire.

R_4 = 1000w.

Resis. of long filt. and leads = $1{\cdot}263 \times \frac{1000}{440} \times 1{\cdot}263 \times 10^{-2} \times 101{\cdot}2 = 2{\cdot}90$

=

" " short " " " = $1{\cdot}263 \times 41{\cdot}2 \times 10^{-2}$

= 0·52

" " mid portion of long filt. = 2·38

Ratio. Resis. $\frac{\text{Resis at 440w balance}}{\text{Resis at } 0^\circ C} = \frac{2{\cdot}38}{0{\cdot}593}$

= 4·02

Temperature (from curves) = 605°C

= 878°A.

To reduce rates of reaction to the value of the rate due to the central portion of the longer filament, a correction of 4%, found by the method previously outlined, had to be made. The bridge currents for filaments of 0·1 mm. diameter ranged from 0·3 to 1·5amp. Whenever a new filament was put into use it was subjected to a thorough outgassing by heating to a red heat for several hours in vacuo less than 10^{-5}mm. In later experiments the filament was glowed for a short period (c. 30 sec) in vacuo between runs. The resistance temperature curves for the molybdenum and tungsten wires used, were determined by the following method:-
A long spiral filament of wire was set up with nickel leads in a form which could be placed in an electric

furnace. In order to balance out the resistance of the leads at the various temperatures, there was placed beside the assembly a similar support on which the filament was shortened. The resistances of the filament and leads, and the leads alone at various temperatures were found by means of a simple Wheatstone bridge arrangement. Temperatures were measured by means of two silica thermometers.

The results are given in table A. See also graphs

(1) Tungsten filament 29·5 cm. long, 0·1mm.dia.

Temperature.	Resistance of filament. rt. in ohms.	$\frac{r^t}{r^o}$
0°C	2·33	1
467	7·65	3·28
515	8·29	3·56
555	8·89	3·81
408	6·95	2·98
262	4·88	2·10
355	6·28	2·69
309	5·73	2·46
12	2·51	1·08

(2) Mo wire 30cm, 0·1mm. dia.

1·5	2·05	1·00
16	2·17	1·06
352	5·35	2·66
561	8·02	3·95
496	7·33	3·57
444	6·89	3·36
404	6·40	3·12
244	4·64	2·36

Although molybdenum and tungsten were used entirely in these experiments, one or two runs were attempted with nickel wire and with Vacsteel wire (a Nc - Fe alloy). To decompose the phosphine these had to be heated to about the same temperature as had the Molybdenum and

Tungsten, but they did not survive more than one or two experiments, involving the decomposition of about 5mm. phosphine in a volume of 200cc. The phosphorus appeared to attack the metal rendering it very brittle and finally causing its complete disintegration, presumably owing to the formation of a phosphide. Molybdenum and Tungsten seemed to withstand the reaction for an indefinite period without undergoing any marked change in catalytic activity.

Molybdenum Filament.

Products of Reaction.

There is a pressure increase during the decomposition which can only be due to the formation of hydrogen, but the question arises as to whether all the hydrogen is liberated into the gas phase. Experimental data given below support the view that the decomposition can be represented by the equation, $4PH_3 = P_4(\text{red}) + \underline{6H}$, no appreciable amount of P_2H_4 on any of the soled hydrides of phosphorus being formed. What is more important from the point of view of chain initiator molecules, is the mechanism of the formation of the phosphorus. Although a red deposit appears on the walls of the reaction tube, phosphorus vapour may also be produced. There are therefore two possible end states in which the phosphorus might occur;

(1) Amixture of red phosphorus, white phosphorus, and phosphorus vapour.

(2)Red phosphorus entirely.

Another

Another possibility is the intermediate formation of P_4 or of white phosphorus, since normal P_4 molecules might evaporate offthe filament in the first instance, collide with the walls, and eventually return to the filament where they are altered in some manner so that on striking the walls again, red phosphorus is formed.[1] The formation of red phosphorus from phosphorous vapour (P_4 mols.) has been repeatedly observed in a tube containing a molybdenum or tungsten filament sufficiently hot to decompose phosphine.

To decide the matter, the following experiment was done, which was typical of several. 0·92mm. of phosphine was admitted to the reaction tube, which was surrounded by a carbon dioxide ether bath at $-80^{\circ}C$. The filament was heated until there was no further pressure change: the pressure increase was 0·46mm., thus confirming the equation given above. The hydrogen was pumped off and the bath withdrawn to allow any white phosphorus to evaporate. 0·63mm. of oxygen was added but no glow could be observed nor was there any observable pressure change. The absence of glow indicated that the pressure of P_4 was less than 2×10^{-3} mm., which is the pressure of P_4 at the lower explosive limit with 0·6mm. of oxygen in a 2cm. tube. Thus no appreciable amount of phosphorus vapour was formed. Had the phosphorus evaporated from the filament, as normal P_4 molecules, these would have been condensed on the cooled glass surface and re-evaporated when the tube was warmed to room temperature. This experiment also provides evidence that there is no intermediate formation of white phosphorus or of phosphorus vapour. The phosphorus must therefore leave the filament in such a form that it condenses on the surface, is adsorbed, and ultimately forms red phosphorus. Now, it has been shown[34,35,36] that P_2 molecules polymerise to red phosphorus on heating a glass surface, and it is therefore probable that the phosphorus leaves the filament as P_2 molecules.

Another confirmatory experiment was done. 6m. of phosphine occupying 200cc. gave a film of red phosphorus which just exhibited interference colours. The film was 10cm. long and the diameter of the tube 2cm., so that it would require at least 3×10^{-2}g. of red phosphorus to produce such a film, whereas 200cc. of phosphine at 6mm. would yield $2{\cdot}4 \times 10^{-3}$g. of phosphorus on decomposition.

A curious effect was noticed during these experiments. Although the film of red phosphorus was usually of uniform thickness, an some instances patches of the reaction tube remained only slightly covered, while in other parts the deposit was dense. It would appear that the walls exert a definite activity towards the formation of red phosphorus. It is of interest, therefore, that not only is the combination of atoms on a wall dependent on its nature, but also in this case the polymerisation of molecules. No experiments have been carried out with walls of different materials, but at certain intervals the reaction tubes were cleaned with aq. bromine water to remove red phosphorus, and were subsequently washed out with water and dried.

As these decomposition experiments are preliminary to the study of the oxidation at pressures below the lower explosion limit, the pressure of phosphine used ranged from a few mm. down to the lowest pressures which could be accurately measured on the McLeod guage. The general procedure at the higher pressures was to admit phosphine to the desired pressure switch on the filament current, and take pressure readings at convenient time intervals. Care was taken during the run to see that the reading on the galvanometer G (Fig. 2) did not move appreciably from zero. This was done by slowly altering R_6 during the run. About 3 seconds was sufficient time to heat the filament up to the desired temperature. As a slight lag was noticeable on the galvanometer, care had to be taken during the heating up that the initial surge of current did not heat the filament too much, even though the galvanometer did not swing over to the side representing a too high filament temperature. On heating up the filament there is a small pressure increase due to heating up of the gas. A correction has to be applied to the observed pressure in order to find the true value at the temperature of the walls of the reaction tubes; this was measured by filling the reaction tube with oxygen and finding the pressure increase on heating the filament to the temperature at which it will subsequently be used. This procedure was repeated for different pressures. Oxygen has nearly the same thermal conductivity as phosphine and does not react with the filament at the temperatures used for decomposition of phosphine. A similar series of experiments were done with hydrogen. As the correction for oxygen was only double that for hydrogen, a linear relation was considered to be sufficiently accurate when calculating the correction for mixtures of the two. The appropriate correction could then be applied for the phosphine hydrogen mixture, as the hydrogen accumulates during the reaction. For a 1 : 1 mixture, therefore, the correction factor would be the mean of those for phosphine and hydrogen alone.

A typical series of pressure time observations, at a number of different initial phosphine pressures, is given in Table 1, $t_{\frac{1}{2}}$ being the time taken to decompose half the phosphine originally present. All pressures are in mm. of mercury, and times t in minutes; column 2 (PH_3 H_2) is the actual observed pressure and is the pressure increase corrected for the small heating effect.

TABLE I.
Experiment 59.

t	$p_{PH_3+H_2}$	Δp	$\Delta p/t$	t	$p_{PH_3+H_2}$	Δp	$\Delta p/t$
0	0·67	0	-- --	3·0	0·90	0·21	0·070
0·5	0·74	0·04	0·08	3·5	0·92	0·23	0·066
1·0	0·78	0·07	0·07	4·0	0·93	0·24	0·060
1·5	0·81	0·10	0·07	4·5	0·94	0·25	0·056
2·0	0·84	0·15	0·075	5·0	0·95	0·26	0·052
2·5	0·86	0·17	0·068	5·5	0·96	0·27	0·049
3						0·34	

$t_{\frac{1}{2}}$ = 2·4 min.

Experiments 59-63 are preliminary experiments using single filament.

Length of Molybdenum filament, 14.9 cm; diameter of filament, 0.01 cm.; temperature of filament, 464°; volume of reaction tube, 90 c.c.; temperature of reaction tube, 20° C.

Experiment 60.

t.	$p_{PH_3+O_2}$	Δp	$\Delta p/t$
0	1·16	0	--
0·5	1·25	0·04	0·08
1·0	1·30	0·09	0·09
1·5	1·34	0·13	0·087
2·0	1·38	0·17	0·085
2·5	1·41	0·21	0·084
3·0	1·44	0·24	0·080
3·5	1·47	0·27	0·077
4·0	1·50	0·30	0·075
5·0	1·56	0·37	0·074
6·0	1·62	0·43	0·071
8·0	1·68	0·49	0·061
10·0	1·73	0·54	0·054
12·0	1·75	0·56	0·047
		0·58	

$t_{\frac{1}{2}}$ = 3·6 min.

Experiment 61.

t.	$p_{PH_3+O_2}$	Δp	$\Delta p/t$
0	2·01	0	--
0·5	2·12	0·02	0·040
1·0	2·17	0·07	0·070
1·5	2·22	0·13	0·087
2·0	2·27	0·18	0·090
3·0	2·34	0·25	0·081
4·0	2·42	0·34	0·085
5·0	2·50	0·42	0·084
6·0	2·57	0·50	0·081
7·0	2·65	0·58	0·082
8·0	2·71	0·64	0·080
10·0	2·79	0·73	0·073
12·0	2·85	0·79	0·066
14·0	2·90	0·84	0·060
		1·00	

$t_{\frac{1}{2}}$ = 6·0 min.

Experiment 62.

t.			
0	2·74	0	--
0·5	2·86	0·01	--
1·0	2·93	0·07	0·07
1·5	2·95	0·10	0·067
2·0	3·01	0·16	0·080
3·0	3·11	0·27	0·090
4·0	3·20	0·36	0·090
5·0	3·31	0·48	0·090
6·0	3·38	0·55	0·091
8·0	3·52	0·69	0·086
10·0	3·68	0·85	0·085
12·0	3·79	0·97	0·081
14·0	3·88	1·06	0·075
16·0	3·97	1·15	0·072
18·0	4·00	1·19	0·067
20·0	4·03	1·22	0·061
		1·37	

$t_{\frac{1}{2}}$ = 8·0 min.

Experiment 63.

t.			
0	3·58	0	--
0·5	3·79	0·06	0·120
1·0	3·86	0·13	0·130
1·5	3·89	0·17	0·113
2·0	3·94	0·22	0·110
3·0	4·01	0·29	0·097
4·0	4·14	0·43	0·107
6·0	4·33	0·63	0·105
8·0	4·48	0·78	0·099
10·0	4·62	0·93	0·093
12·0	4·78	1·10	0·092
14·0	4·88	1·20	0·086
16·0	5·00	1·33	0·083
19·0	5·08	1·41	0·074
		1 79	

$t_{\frac{1}{2}}$ = 9·5 min.

The first characteristic to be noticed about these results is that the time of half life increases with increase of phosphine pressure. Similarly, the initial rate of reaction is maintained and does not decrease until a large fraction of the phosphine is decomposed. Further, the initial rate only increases 50% for an increase in original phosphine pressure of from 0·67 to 3·58mm.

The effect of hydrogen was next investigated to find whether it might modify the course of the decomposition as it accumulates in the system: no influence could be measured as is seen from the following series of results:-

Expt.	PH_3	H_2	$t_{\frac{1}{2}}$
24	1·98	--	1·6
25	1·92	0·92	1·9
26	1·84	1·79	1·8
28	2·01	--	1·6
29	1·84	2·90	1·5

From the foregoing results it may be concluded that at pressures of the order of a few mm. of mercury the course of the decomposition conforms nearly to a reaction of zero order. This suggests that the phosphine is becoming adsorbed on the surface and that the decomposition is taking place there.

The deviation of the above results from a reaction of zero order, suggested that at lower pressures adsorption of phosphine might be so much less marked, that the reaction would become unimolecular. Experiments using the McLeod guage as manometer were therefore done. For this the procedure had to be modified to a certain extent: phosphine to the required pressure was passed into the reaction system and the filament switched on at the desired temperature for a given time, after which the pressure was determined. This was repeated until most of the phosphine was decomposed. Conditions were arranged that the time taken to heat the filament to its working temperature was about 2% of the time of reaction. Even so, zero time was about two seconds after the filament current had been switched on, and about one second before it attained its constant temperature. The volume of the McLeod guage and connections was determined so that the observed velocity could be reduced to the value obtained in the reaction tube used in the high pressure experiments.

TABLE II gives a typical series of runs using the same filament and temperature as in TABLE I: k is the unimolecular coefficient, $1/t.\log_{10}\frac{a}{a-x}$, where a is the initial pressure of phosphine, and x that of phosphine decomposed after time t. Volume of apparatus was 390c.c., $t'_{\frac{1}{2}}$ is time of half life in volume of 90c.c.

TABLE II.

Conditions of filament same as those in TABLE I.

t.	$PH_3 + H_2$	Δp	k	Δp/t.
		Experiment 67.		
0	0.1240	0	--	--
1	0.1450	0.0210	0.178	0.021
2	0.1585	0.0345	0.176	0.0173
3	0.1690	0.0450	0.180	0.0150
4	0.1755	0.0515	0.193	0.0129
6	0.1825	0.0585	0.209	0.0098
8	0.1835	0.0595	--	0.0074
		0.0620		

$t_{\frac{1}{2}}$ 1·8 min., $t'_{\frac{1}{2}}$ 0·42 min.

t	$PH_3 + H_2$	Δp	k	Δp/t.

Experiment 68.

0	0·0695	0	--	--
1	0·0845	0·0150	0·246	0·0150
2	0·0925	0·0230	0·236	0·0115
3	0·0970	0·0275	0·227	0·0092
4	0·0985	0·0290	0·196	0 0072
6	0·1000	0·0305	0·133	0·0051
8	0·1115	0·0320	0·146	0·0040
		0·0347		

$t_{\frac{1}{2}}$ 1·35 min.; $t'_{\frac{1}{2}}$ 0·313 min.

Experiment 69.

0	0·0385	--	--	--
1	0·0490	0·0105	0·342	0·0105
2	0·0520	0·0135	0·263	0·0067
3	0·0550	0·0165	0·282	0·0055
4	0·0565	0·0180	0·297	0·0045

$t_{\frac{1}{2}}$ 1·08 min.; $t'_{\frac{1}{2}}$ 0·251

Experiment 70.

0	0·0190	--	--	--
1	0·0235	0·0445	0·278	0·0045
2	0·0270	0·0080	0·217	0·0040
3	0·0275	0·0085	0·328	0·0028
4	0·0277	0·0087	0·259	0·0022
		0·0095		

$t_{\frac{1}{2}}$ 0·95 min.; $t'_{\frac{1}{2}}$ 0·220 min.

Experiment 71.

0	0. 0060	0	--	--
1	0. 0080	0· 0020	0· 176	0· 0020
2	0. 0085	0· 0025	0· 38	0· 0013
3	0. 0087	0· 0027	0· 33	0· 0009
4	0. 0087	0· 0027	--	0· 0007

$t_{\frac{1}{2}}$ 0·70 min.; $t'_{\frac{1}{2}}$ 0·162 min.

Even at quite low pressures the time required for half decomposition is slightly dependent on pressure, but the approximate constancy of the values in column 4 of Table II indicates that the reaction is nearly unimolecular. The value of $\Delta p/t$ drifts considerably as is to be expected.

If the reaction were of zero order, then on plotting log $t_{\frac{1}{2}}$ against log p, a straight line of unit slope should be obtained, whereas a unimolecular reaction would give a line parallel to the log p axis, since $t_{\frac{1}{2}}$ would be independent of pressure. Such a plot has been made in fig. 3 from the results in Tables I and II. At higher pressures the slope of the curve is unity, but gradually decreases until at 0·005 mm. it is nearly zero. The curve could not be extended to much higher pressures since the half life period would have been several hours. On the other hand, had the reaction rate been increased by raising the temperature of the filament, the order would have risen owing to evaporation of adsorbed phosphine and consequently a much higher pressure would be required to approach the zero order reaction. This can be seen from the results shown in fig. 4.

Temperature Coefficient.

The measurement of the temperature coefficient of the reaction, owing to its transitional character, allows of the estimation of two quantities. First, the energy of activation (E) of the reaction on the Molybdenum surface can be calculated from the variation of $t_{\frac{1}{2}}$ with temperature from the usual formula $d \log (1/t_{\frac{1}{2}})/dT = E/RT$. The apparent energy of activation (Q) of the unimolecular reaction is composed of two terms: the energy of activation ([illegible]) on the surface minus the heat of desorption (λ) of the adsorbed phosphine. Since Q is easily measured λ can be calculated. In the transition reaction Q will vary between these limiting values. It has been seen that at the low pressure of 0·005 mm., the reaction is not quite of the first order: hence in determining the temperature coefficient, two sets of experiments were made. In the first the temperature of the filament was maintained constant, the variation of half life with pressure plotted, and the curve extrapolated to zero pressure. Another similar series of observations was made for another temperature, and the results also extrapolated to zero pressure of phosphine. The ratio of $t_{\frac{1}{2}}$ for zero pressure for the two temperatures was used to calculate Q.

Table III contains the data for this calculation, and fig. 4 shows $t_{\frac{1}{2}}$ plotted against phosphine pressure.

TABLE III.

Temperature of reaction tube 20°; Temperature of filament in (a) 645°; in (b) 574°.

(a) Values of $PH_3 + H_2$.

t.	Expt. 73.	Expt. 74.	Expt. 75.	Expt. 76.	Expt. 77.
0	0·0255	0·0445	0·1310	0·0580	0·0865
1	0·0330	0·0515	0·1515	0·0685	0·1040
2	0·0347	0·0575	0·1650	0·0775	0·1120
3	0·0367	0·0605	0·1770	0·0805	0·1200
4	0·0375	0·0635	0·1850	0·0845	0·1255
5	--	0·0650	0·1915	0·0855	0·1270
6	--	--	--	--	--
7	--	--	--	--	--

(b)

t	Expt. 78.	Expt. 79.	Expt. 80.	Expt. 81.
0	0·0610	0·0955	0·1365	0·0410
1	0·0660	0·1030	0·1465	0·0455
2	0·0695	0·1075	0·1515	0·0485
3	0·0735	0·1120	0·1585	0·0515
4	0·0760	0·1175	0·1625	0·0525
5	0·0805	0·1215	0·1700	0·0540
6	0·0810	0·1255	0·1735	--
7	--	0·1280	0·1815	--

t	Expt. 82.	Expt. 83.	Expt. 84.
0	0·0117	0·0130	0·1090
1	0·0133	0·0157	0·1145
2	0·0157	0·0160	0·1175
3	0·0160	0·0173	0·1220
4	0·0163	0·0187	0·1265
5	--	--	0·1275
6	--	--	0·1310
7	--	--	--

In experiment 84, 0·0385 mm. of hydrogen was present initially and as seen from fig. 4, $t_{\frac{1}{2}}$ lies on the curve, so hydrogen has no effect on the low pressure decomposition.

The value of Q has been calculated from the curves in fig. 4 at different phosphine pressures, and it is seen that Q gradually increases with PH_3.

PH_3	$\frac{\text{Rate 1}}{\text{Rate 2}}$	Q (kg.-cal.)
0	2·00	15·1
0·02	2·24	17·5
0·06	2·61	20·8
0·10	2·79	22·3
0·20	2·80	22·3

Figs. 3 & 4 show that at the lower temperature 464° the reaction is not unimolecular, whereas at the higher temperature, where phosphine is much less strongly adsorbed, unimolecular characteristics are more closely obeyed, i.e., $t_{\frac{1}{2}}$ is nearly independent of PH_3. Measurements of the temperature coefficient were also made at higher pressures with the results given in table IV.

TABLE IV.

Temperature of reaction tube 17°. Volume of apparatus and filament as in Table 1.

Expt.	PH_3	$t_{\frac{1}{2}}$	Temperature of filament.
44	1·97	23	420°
45	1·91	18	420
46	2·19	15	428
47	1·96	6·1	448
49	1·92	1·35	497
52	1·96	5·2	459
53	1·92	11·6	435

Energy of activation E = 39·3 kg.-cal.

The heat of desorption of the phosphine is thus 39·3 - 15·1 = 24·2 kg.-cal. As this value is essentially calculated by extrapolation af the low pressure results to zero pressure, it represents the heat of desorption of phosphine from an uncovered molybdenum surface.

Tungsten Filament.

Tungsten did not behave an exactly the same way as molybdenum in this reaction. The pressure increase acconpanying the complete decomposition was, however, exactly half the initial pressure of phosphine. Similarly, phosphorus was deposited as the red variety on the walls of the tube. On carrying out experiments similar to those with the molybdenum filament to determine whether white phosphorus was an intermediate product, some traces of it were found, e.g., in one experiment, after the phosphine (0.5mm.) had been decomposed and the reaction tube purified out at a temperature of about -70°C, on admission of a few mm. of oxygen, and on warming to room temperature, there was a bright flash of about 1 sec. duration. There was no succeeding continuous glow and no noticeable change in pressure on the oil manometer. The amount of white phosphorus produced by the reaction was thus estimated to be less than 0.05mm.

Experiments with tungsten were done wholly with a double filament as this method should give a more accurate measure of temperature.

TABLE V·

Temperature of Tungsten filament = 560°C. Lengths 12 cm. and 3 cm.

<u>Experiment 253.</u> Vol.= 324 cc.

t.	PH_3 H_2	PH_3	k
0	0·488	0·488	
1	0·498	0·469	0·018
2	0·506	0·448	0·019
4	0·526	0·413	0·018
8	0·557	0·339	0·020

t/4 <u>6</u>·0min.

<u>Experiment 256.</u>

t.	PH_3H_2	RH_3	K
0	0·967	0·967	
1	0·985	0·910	0·026
2	1·003	0·875	0·022
4	1·037	0·809	0·019
8	1·100	0·701	0·018

t/4 6·4min.

<u>Experiment 257.</u> Pressures measured by McLeod Guage.

t.	PH_3 H_2	PH_3	k
0	0.00855	0.00855	
1	0.00860	0.00845	0.0055
2	0.00915	0.00735	0.033
4	0.00980	0.00585	0.041
8	0.01080	0.00400	0.040

t/4 = 2.8min; t'/4 = 1.6min.

<u>Experiment 260.</u> Vol. = 581 cc.

t.	PH_3H_2	PH_3	k
0	0·1122	0·1122	
1	0·1148	0·1070	0·022
2	0·1183	0·1000	0·025
4	0·1225	0·0916	0·022
8	0·1303	0·0760	0·021

t/4 = 5.6min; t'/4 = 3.1min.

Experiment 261.
Vol. 581 cc.

t.	PH_3+H_2	PH_3	k
0	0·0412	0·0412	
1	0·0434	0·0368	0·049
2	0·0453	0·0330	0·048
4	0·0472	0·0292	0·038
8	0·0505	0·0226	0·033

t/4 = 2.9 min; t'/4 = 1.6 min.

Experiment 271. Using Hg manometer, vol. 121cc.

t.	PH3 H_2	PH_3	k
0	029·0	29·0	
1	30·3	26·4	0·022
2	31·2	24·6	0·025
4	33·3	20·4	0·022
8	37·0	13·0	0·021

t/4 = 3.4; t'/4 = 9.1min.

Experiment 275.
Vol 121 cc.

0	262·5	262·5	
1	276·0	235·5	0·047
2	283·0	221·5	0·037
44	294·0	199·5	0·033
8	311·5	164·5	0·025

t/4 = 4·0; t'/4 = 10·7.

Experiment 278. Oil manometer, vol. 121 cc.

0	0·795	0·795	
1	0·854	0·677	0·070
2	0·904	0·577	0·070
4	0·989	0·407	0·073
8	1·102	0·181	0·080

t/4 = 1·7; t'/4 = 4·5 min.

Experiment 279.
Vol. 121 cc.

0	0·396	0·396	
1	0·429	0·330	0·080
2	0·458	0·272	0·082
4	0·504	0·180	0·085
8	0·558	0·072	0·092

t/4 = 1·5; t'/4

Experiment 280.
Vol. 121 cc.

0	0·099	0·099	
1	0·111	0·075	0·120
2	0·117	0·063	0·098
4	0·130	0·038	0·104
8	0·140	0·018	0·092

t/4 = 1·0; t'/4 = 2·6min.

In Table V the results of a series of experiments are given in which the pressure was varied from 0.00855mm. to .2625 mm. The volume of the apparatus including the particular manometric system in use is shown; the time (t/4) required for the reaction to go 25% of its full extent is given at the bottom of the record of each experiment. t'/4 is the value of t/4 corrected to apply to an apparatus of volume 324 cc. The observed reaction velocity is due to the two filaments.

In order to calculate the rate produced by the central portion of the long filamant t/4 must be increased by 4%. k is unimolecular, veloc. coefficient as in Table II.

First it is noteworthy that t/4 does not markedly depend on pressure. In fact a 30,000 fold pressure only changes t/4 by less than a factor of 10, viz:- from 1.6 to 10.7. The reaction is therefore nearly unimoleculsr as is further shown by the constancy of k in each run.

The following are typical of experiments which were made with a pressure of added hydrogen of the same order as that of the PH_3. No inhibitory action was noted either at high or low pressure.

TABLE VI.

Filament same as Table V. Temperature of filament 658°C.

Experiment 274.

t	PH_3 H_2	PH_3
0	30·0	30·0
1	37·9	14·2
2	39·2	11·6
4	41·0	8·0
8	41·9	6·2

Experiment 276.
31.7m H_2 at start.

t	PH_3 H_2	PH_3
0	61·0	29·3
1	69·0	13·3
2	70·4	10·5
4	71·3	8·7
8	71·9	7·5

Experiment 62.
Temperature 655°C.

0	0·0530	0·0530
2	0·0639	0·0312
4	0·0705	0·0180
6	0·0747	0·0096
9	0·0780	0·0030
12	0·0793	0·0004

t/2 = 2.6 min.

Experiment 58.
Temperature 655°C.

0	0·1033	0·0423
2	0·1124	0·0241
4	0·1167	0·0155
6	0·1204	0·0085
9	0·1227	0·0035
12	0·1240	0·0009

t/2 = 2.7 min.

TABLE VII.

Experiments with constant phosphine pressure and varying temperature.

In these experiments after the run had proceeded for a given time, the filament was switched off, and the P N.C. measured after the PH_3 had been condensed out with liquid air. Time was allowed for condensation and remixing before restarting the runs and corrections for cooling of side tube and v.p. of phosphine made just as in the oxidation experiments.

Vol. of apparatus 324 cc. Length of long filament 12 cm. and of short filament 3 cm.

Experiment 246. Temperature 437°C.

Time in mins.	PH_3+H_2	Δp	k	$\frac{\Delta p}{t}$
0	0·395		0·0005	
4	0·397	0·002	0·003	0·0005
8	0·400	0·005	0·003	0·0006
16	0·408	0·013	0·0025	0·0008

Experiment 247. Temperature of filament 606°C.

0	0·401			
1	0·423	0·022	0·046	0·022
2	0·444	0·043	0·043	0·022
4	0·472	0·071	0·042	0·018
8	0·516	0·115	0·045	0·014

Experiment 248. Temperature of filament658°C

0	0·399			
1	0·435	0·036	0·085	0·036
2	0·467	0·068	0·085	0·034
4	0·521	0·122	0·100	0·030

Experiment 249. Temperature of filament 560°C.

t	PH_3 H_2	Δp	k	$\frac{\Delta p}{t}$
0	0·400			
1	0·412	0·012	0·034	0·012
2	0·443			
4	0·441	0·041	0·030	0·010
8	0·475	0·075	0·025	0·009

Experiment 250. Temperature of filament 495°C

0	0·404			
2	0·411	0·007	0·006	0·0035
4	0·416	0·012	0·006	0·003
8	0·425	0·021	0·006	0·0025
16	0·442	0·038	0·0055	0·0024

From the above values of k and temperature, the value of Q - Decomposition on Tungsten - is 23.6 Kg.Cal.

In order to find if Q varied over a range of pressure, as in the case of Molybdenum, experiments were done to find E at both high and low pressures.

Low pressure results.

		PH_3	Temp. of filament. 1.	2.	Half-life(sec)
Expt.	77	0·0685	523°C	407°	192
	78	0·0675	482°C	359°	492
	80	0·0596	560°C	441°	96

From these results Q = 23.8 Kg Cal

High pressure results.

Expt.	86	4·37	560°	441°	120
	89	4·59	523°	407°	240
	90	4·36	482°	359°	720
	91	5·19	415°		3000

Q = 25.8 Kg. Cal.

In Table VII are given three series of results at different pressures over a range of filament temperature. The energies of activation Q are practically identical, and therefore in agreement with the fact that the reaction is unimolecular over this range of pressure.

The temperatures given under (2) were calculated by the old method of measuring the resistance and assuming a constant temperature along the whole length of the wire; The calculations by the new method (1) are appreciably higher. The discrepancy is shown more clearly by a calculation of Q. The first and third r results of the low pressure experiments give Q = 28.7 Kg.cal, whereas the lower temperature gives Q = 18.7 Kg.cal. Although the absolute value of the temperature and energy of activation is not at present of any great theoretical importance, yet the discrepancy might alter the significance of any theoretical discussions in comparing similar reactions catalysed by filaments of different materials.

THE EFFECT OF ATOMIC HYDROGEN ON THE CATALYTIC DECOMPOSITION OF PHOSPHINE AND AMMONIA.

In the photo-chemical experiments on the decomposition of phosphine,[31] it was shown that atomic hydrogen can react with the transitory intermediate products of the dissociated molecule to reform phosphine; similar effects were obtained with ammonia by Melville.[43] It was suggested that the inhibition was due to the reaction $H \quad PH_2 \ (NH_2) \quad PH_3 \ (NH_3)$ occurring at the walls of the reaction tube. Now, if the decomposition of these phosphine and ammonia molecules with the production of surface compounds of the nature $W - PH_2$ or $W - PH$, then it should be possible, in principle, to bombard with hydrogen atoms the filament upon which phosphine or ammonia is being dissociated, and so retard the rate of decomposition. The result of such an experiment is somewhat difficult to interpret for phosphine, since the possibility of reduction of the phosphorus in the gas phase or at the walls before condensation to the red modification, must be considered.

The experimental procedure was similar to that adopted in the decomposition experiments (246 - 250), the atomic hydrogen being produced by collision with an optically excited mercury atom. The reaction tube in fig. 1 was replaced by one of silica, 2.5 cm. in diameter, whilst the filament assembly remained the usual three point arrangement. This tube was joined to the apparatus by means of a silica-glass ground joint, and in order to keep the concentration of mercury atoms constant, a small drop of mercury was placed in the tube. The mercury lamp (water cooled) was set up about 10 cm. from the tube and a shutter fixed between it and the tube. The phosphine was first of all admitted to the tube, measured on the oil manometer, and then condensed out with liquid air. The hydrogen was then admitted and the two gases allowed to mix, and the total pressure read on the manometer. Runs were thus done with both filament and lamp simultaneoul eously (FL), with the filament alone (F), and with the lamp alone (L). At the end of each the phosphine was condensed out, and P.N.C. found. It was not possible to use the oil manometer with ammonia, as this gas dissolves appreciably in the oil. Also, as pointed out before, a nickel filament could not be used for phosphine owing to disintegration. Care was taken that the run LF was done before the run F, so that any decrease in rate caused by the lamp cannot be due to the deposition of phosphorus cutting down the light supply. Some results are given in Table XVIII.

TABLE XVIII.

Gas	Filament	Time of run.	PH_3NH_2	PH_2	$PH_3(NH_2)$	Conditions.
PH_3	Mo.	5	0·286	0·636	0·124	L
	Mo.	5	0·292	0·636	0·189	LF
		5	0·295	0·633	0·248	F
NH_3	Mo.	2	2·06	4·06	1·44	F
		2	1·83	4·20	0·00	L
		2	1·83	4·20	0·90	LF
PH_3	Mo.	2	1·92	5·58	1·62	F
		2	1·92	5·38	1·14	FL
		2	1·77	5·88	0·07	L
NH_3	W.	2	2·04	4 04	1·14	F
		2	1·93	4 02	0·01	L
		2	1·84	4 12	0·67	L F
PH_3	W.	2	1·84	3·66	0·87	FL
		2	1·91	3·59	0·09	L
		2	1·96	3·60	0·84	F
NH_3	Ni	2	1·87	3·74	0·29	F
		2	1·95	3·57	0·15	FL
		2	1·95	3·57	0·00	L
PH_3	W.	4	0·278	0·582	0·153	LF
		4	0·298	0·580	0·048	L
		4	0·283	0·582	0·186	F
		4	0·308	---	0·111	L

An inspection of this table reveals that in each set of experiments both with tungsten and molybdenum and nickel filaments, the amount of gas decomposed by the filament and lamp simultaneously is less than that when these agents are operated separately, i.e. atomic hydrogen retards the decomposition.

DISCUSSION.

The results may be summarised as follows. At pressures less than 0.1 mm. and at the temperature of the experiments, phosphine decomposes according to a unimolecular law on tungsten and molybdenum filaments; the rate of reaction is unaffected by the presence of molecular hydrogen. No inhibitory influence of phosphorus can be detected. This is simply explained by the fact that as soon as it leaves the filament surface it is removed from further possible action by condensation in the red form on the walls of the reaction tube. It is also seen from the results that the activities of the two catalysts, tungsten and molybdenum, appear to be of the same order of magnitude. On increasing the pressure of phosphine, its adsorption on molybdenum increases rather more rapidly than on tungsten, so that with the former filament the reaction tends to be of zero order, whilst the unimolecular law is still valid for the latter.

As these filaments function at comparatively low temperatures, it is improbable that the hydrogen liberated during reaction is anything but normal molecules, possessing translational energy corresponding to the temperature of the wire. Such a molecule is therefore unlikely to have sufficient energy to enable it to initiate a stable chain reaction between phosphine and oxygen. In the case of the phosphorus it must be different, for when P_4 molecules derived from white phosphorus condense on a cold surface, they do not in general condense to the red modification. Hence the molecules of phosphorus evaporating from the filament are not normal P_4 molecules.

In a paper by Melville[34.] mention has been made of experiments in which phosphorus vapour at low pressure has been passed through a silica jet at 700°C, and the resulting molecules projected by means of another cool jet on to a glass surface at -80°. This experiment gave rise to a deposit of red phosphorus on the cooled surface. Now, it has been shown by Preuner and Brockmoller[35.] by vapour density measurements, that when normal P_4 molecules are heated, P_2 molecules are produced. This has been verified by absorption band spectrum measurements of Jakolewa.[36.] Thus it is shown that red phosphorus is formed when P_2 molecules condense on a cool glass surface. The temperature of the filament in the present experiments is quite sufficient to dissociate P_4 molecules. Further, in experiments on the initiation of chains in phosphorus oxygen mixtures by hot filaments, it was observed that mere heating of a tungsten or molybdenum wire to 500° in phosphorus vapour produced a deposit of red phosphorus on the reaction tube. It may reasonably be concluded, therefore, in absence of evidence to the contrary, that

P_2 molecules evaporate from a filament upon which phosphine molecules are being decomposed. The question then arises as to whether these P_2 molecules can initiate a chain reaction between phosphine and oxygen. This question is dealt with in the next section of this thesis.

There is, as might be expected, a general similarity between the decomposition of ammonia and of phosphine. In accordance with the relatively greater stability of the former the temperature to which the filament must be raised, in order to obtain a measureable rate of reaction, is higher for it than for phosphine; *e.g.*, on tungsten, phosphine has a half life period at 500°C similar to that of ammonia at 1000°C, as found by Kunsman[40,41,42.] in an apparatus of similar dimensions. Nevertheless, it is surprising that the decomposition of phosphine on tungsten is unimolecular at pressures where zero-order conditions obtain for ammonia. The ammonia is therefore much more strongly adsorbed. It would be of interest to compare the heats of evaporation (λ) of the two gases for the same filament by measuring the temperature coefficient of the reactions over a wide range of pressures in order to find whether $\lambda(NH_3)$ is greater than $\lambda(PH_3)$. At low pressures both reactions are unimolecular.

With a molybdenum filament both gases at high pressures decompose according to a zero order law. No results for ammonia on this metal at low pressures are available, but in Kunsman's results for ammonia on molybdenum at different temperatures, a plot of the logarithm of the time required for half decomposition against the reciprocal of the absolute temperature gives a curve which shows a decrease in the apparent energy of activation at high temperatures. This curvature is possibly due to the smaller adsorption of the gas at high temperatures, whereby the order of the reaction increases from zero to unity.

According to Kunsman's results for ammonia, one difference between phosphine and ammonia is that hydrogen does not inhibit the decomposition of the former, whereas with the latter inhibition is pronounced both at high and low pressures. These results are however questioned by Hailes,[45.] who found that in the case of ammonia there is no deceleration of reaction rate due to hydrogen. He also suggests that the falling off in rate of reaction observed by Kunsman was due to the reduction in ammonia pressure caused by decomposition.

If the surface of the catalyst is catalytically uniform and if any displacement of adsorbed reactant by hydrogen were considered to be the means whereby the retardation takes place, then it is not to be expected that there should be any difference between the effect of hydrogen on the decomposition of the two gases. However, assuming retardation by hydrogen in the ammonia decomposition, the discrepancy could be explained in either of the following ways:-

1. The catalyst is not of uniform activity and

the ammonia decomposes on centres which can easily be covered with hydrogen, whereas different active centres for phosphine are not affected by hydrogen.

2. Hydrogen not only displaces ammonia, but after or as a consequence of being adsorbed, it becomes sufficiently reactive to attack the intermediate products of decomposition of the ammonia molecule and to regenerate ammonia. In the second case then, inhibition by hydrogen would be due essentially to a chemical reaction, and it is therefore reasonable to suppose that there would be a marked difference in the condition for the appearance of inhibition.

More evidence showing that any inhibition should be due to a mechanism similar to case 2 above is seen in Table XVIII. Here it is seen that the simultaneous production of atomic hydrogen with the dissociation of ammonia or phosphine leads to a retardation of the latter process. This result is to be expected for ammonia, as, if Kunsman's results are to be believed, molecular hydrogen is an inhibitor for the decomposition. The dissociation of H_2 by means of excited mercury atoms no doubt facilitates adsorbtion, for it virtually removes the necessity of activation which is required when a normal H_2 molecule collides with the catalyst. The inhibition must accur on the surface of the wire since atomic hydrogen does not attack molecular nitrogen in the gas phase. The hydrogen atoms probably react with the surface compounds M - NH or M - NH_2.

which are formed during the decomposition.[44]

That a similar mechanism holds for phosphine is probable from the following argument. If a mixture of phosphorus and mercury vapour is illuminated by a mercury lamp, there is a deposition of red phosphorus. The P_4 molecules are therefore changed in some way, probably to P_2 molecules, that they undergo the allotropic transformation. If hydrogen is present also, no appreciable amount of phosphine is produced,[45] that is, atomic hydrogen does not attack these reactive molecules derived from P_4. If the same molecules give rise to the red phosphorus in the thermal decomposition experiments, then it is improbable that atomic hydrogen can react with them to give phosphine. The retardation which is observed must therefore have taken place on the surface of the filament itself in a similar manner to the ammonia reaction. It would be somewhat surprising, in view of the similarity in the behaviour of atomic hydrogen with respect to ammonia and phosphine, if in the former case inhibition by molecular hydrogen were present. It is possible that the difference may be due to the fact that the higher temperature of the filament, necessary for decomposition of ammonia, supplies energy of activation required by a normal H_2 molecule, before adsorbtion can take place.

The energies of activation (E) for the decomposition of ammonia on tungsten, molybdenum, and nickel are all of the same magnitude, *viz*, 45 Kg.-cal,[40] which is higher than the values for phosphine. Other results by Hinshelwood and Burk[47] give results of about 37 Kg.-cal. These values were taken at pressures of about 100 mm. of ammonia. Later results by Hailes[45] at lower pressures give results appreciably smaller than 45 Kg.-cal. He points out that the apparent energy of activation (Q) consists of two quantities, *viz.*, the heat of adsorption A, and the energy of activation E (CF. the decomposition of phosphine on molybdenum). The heat of adsorption (λ) increases as the degree of saturation of the surface decreases.[46] Thus at low pressures Q decreases and is about 27 Kg.-cal at pressures of a few mm., which does not greatly differ from that of phosphine under similar conditions.

THE OXIDATION OF PHOSPHINE ON TUNGSTEN AND MOLYBDENUM FILAMENTS.

In the first part of this thesis the kinetics of the thermal decomposition of phosphine on tungsten and molybdenum were investigated. This was done as a preliminary to the study of the oxidation at pressures below the lower critical explosion limit. The purpose of the present experiments was to determine if the oxidation was a chain reaction, the chains being started on the filament and terminated on the walls.of the reaction vessel as in the case with phosphorus-oxygen mixtures.[37] Further it was suggested in the discussion on the mechanism of the formation of the red phosphorus in the decomposition, that P_2 molecules may evaporate off the filament. As it has been shown that P_2 molecules initiate chains in $P_4 - O_2$ mixtures[38], it was expected that they might also provide reaction centres for the chain oxidation of phosphine. On the other hand, as oxygen is strongly adsorbed on a tungsten surface, it is possible that the decomposition of phosphine would be markedly inhibited and that the phosphorus formed would undergo a purely surface oxidation without giving rise to chain initiator molecules. There are a number of other possibilities but they need not be detailed until the results have been discussed.

Three criteria exist whereby the chain character of the reaction may be recognised:-

(a) The appearance of a glow, the intensity of

which

is proportional to the rate of oxidation.

(b) The acceleration of the reaction rate by the use of wider reaction bulbs, and

(c) The acceleration produced by the addition of inert gases to the reaction mixture. These three criteria are fulfilled in the oxidation of phosphorus.

Suppose, however, that an appreciable part of the reaction took place on the surface of the filament, exclusive of the small proportion of the heterogeneous reaction required to start the chains. The glow would still be observed, but the rate of the reaction would no longer be proportional to the square of the reaction vessel diameter, (as in the case of a chain reaction) nor would the acceleration by inert gases be so marked. Owing to difficulties arising from the variability of the surfaces of reaction bulbs of differing diameters, it is sometimes not easy to verify the diameter law, and therefore in this case the inert gas effect has been used to determine what fraction, if any, of the reaction consists of a chain process. This acceleration by inert gases can be calculated from experiments on the effect of the gas on the lower explosion limit,[39.] for it has been shown in the phosphorus experiments that the observed increases in velocity are in agreement with the values calculated from the diffusion theory.

EXPERIMENTAL.

Apparatus. The apparatus was the same as that used in the first part of this thesis, and the divided filament method was used to measure the temperature of tthe filament. The pressures that could be employed were, of course, now restricted by the occurrence of explosion at about 0.9 mm. - 1 mm. for the 1:1 mixture. An oil manometer was used for the majority of the experiments. Its range was 1.26 mm., using a microscope to read the level of the oil and the sensitivity of this arrangement gave each reading correct to ± .002mm. or better. Both molybdenum and tungsten were apparently unattacked by the reactants or the products of reaction, for, on examination of the filament surfaces by means of a microscope, no pitting or roughening could be observed, and the diameter as measured by a micrometer remained the same throughout a long series of experiments. It was observed, however, that the activity of the wire gradually fell off with use, but could easily be restored by heating the wire to about 1000°C in vacuo by means of an electric current. Between each run the filament was glowed at this temperature with the pumps on for about 30 seconds, and, as can be seen from the experimental results below, the adoption of this procedure kept results reproducible within fairly close limits.

A difficulty appears when the method of measuring the rate of reaction is considered, for the nature of the products depends on the relative proportions of the phosphine oxygen mixture. When oxygen is in deficit, the reaction is mainly

$$PH_3 + O_2 \rightarrow HPO_2 + H_2$$

as can be seen from the fact that the pressure at the end of an experiments using a 1:1 mixture is just half the original total pressure of reactants. (~~Expt~~.). With a large excess of oxygen a more highly oxidised form of phosphorus acid is obtained and the amount of hydrogen produced is not proportional to that of the oxygen used up. With equivalent proportions, the rate might be measured by finding the decrease in phosphine or oxygen pressure. Another, and simpler, method, as HPO_2 has an inappreciable vapour pressure as measured by the oil manometer, is to follow the reaction by means of the decrease in total pressure during its course.

The total pressure during a run, however, does not give a true estimate of the rate of reaction. This can be seen from experiments 158 to 164, Table VIII, where, with constant phosphine pressure, at low oxygen pressures, there is an increase in total pressure during reaction, whereas at higher oxygen pressures the change is a decrease in pressure.

TABLE VIII.

Mo. filament, total length 15 cm., 0.01 cm. in diameter.
Temperature 563°C*, Volume of apparatus 230 cc.

	158.	161.	162.	163.	164.
	initial				
PH_3	0.432	0.429	0.411	0.434	0.429
O_2	0.407	0.303	--	0.199	0.101
Time	total pressure.				
0	0.839	0.732	0.411	0.633	0.530
1	0.820	0.727	0.429	0.636	0.542
2	0.800	0.715	0.445	0.635	0.548
4	0.758	0.699	0.474	0.636	0.564
8	0.702	0.675	0.524	0.640	0.591
16	0.--	0.622	0.583	0.625	0.610

To find which of the methods would prove most suitable, analyses were made of the PH_3 - H_2 - O_2 mixtures at various stages in the reactionsand with differing initial proportions of phosphine and oxygen. The phosphine was removed with liquid air and the hydrogen-oxygen mixture withdrawn by the Töpler pump into a small tube, fitted with a platinum filament and containing calcium chloride. The filament was heated until there was no further pressure change. Oxygen was then added and another combustion carried out, in order to determine whether the residual gas after the first combustion was hydrogen or oxygen.

Table IX gives the complete results for a number of runs using a molybdenum filament.

The procedure in experiments 172 - 189 was as follows: Phosphine was passed into the reaction tube and its pressure measured. This was then condensed out into the side tube and oxygen was then added. The phosphine was then allowed to evaporate and when the side tube had warmed to room temperature, the total pressure of gas was read on the oil manometer. The initial oxygen pressure was then found by difference. (To admit the oxygen in well regulated quantities it was found suitable to use a two way tap, with the central limb sealed off short and the straight bore sealed up, as a pipette). The filament was then heated for the required time and the pressure again determined. Liquid air was applied to the side tube to condense

Filament and apparatus as Table VIII.[*]

TABLE IX.

Expt. No.	Reaction Time.	PH_3	O_2	Final press.	Δp	p NC	ΔPH_3	$p\ H_2$	$p\ O_2$
172	8	0.425	0.406	0.515	0.316	0.364	0.274	0.305	0.059
173	4	0.416	0.405	0.557	0.264	0.371	0.230	0.253	0.118
174	2	0.415	0.394	0.633	0.176	0.371	0.151	0.220	0.151
175	1	0.415	0.395	0.685	0.125	0.374	0.104	0.133	0.241
176	1	0.405	0.200	0.567	0.038	0.200	0.037	0.089	0.110
177	2	0.400	0.199	0.544	0.055	0.212	0.068	0.136	0.076
178	4	0.409	0.188	0.531	0.066	0.231	0.109	0.159	0.073
179	8	0.409	0.197	0.517	0.089	0.286	0.178	0.220	0.066
181	1	0.412	0.098	0.497	0.013	0.105	0.020	0.062	0.042
182	2	0.416	0.097	0.494	0.019	0.133	0.055	0.089	0.044
183	4	0.400	0.097	0.476	0.021	0.160	0.084	0.119	0.041
184	8	0.409	0.097	0.486	0.020	0.221	0.144	0.148	--
186	1	0.413	0.784	0.874	0.322	0.660	0.198	0.196	0.466
187	2	0.416	0.778	0.756	0.443	0.611	0.276	0.181	0.429
188	4	0.411	0.768	0.628	0.551	0.557	0.340	0.215	0.342
189	8	0.411	0.753	0.582	0.582	0.546	0.375	0.230	0.316

The measured reaction velocity is due to both filaments.

[*] Temperature of the central portion of the long filament.

out the phosphine in order to find the pressure of H_2 and O_2. A standard time of four minutes was usually allowed for this operation, but this time was increased for large non-condensable pressures. As the vapour pressure of phosphine at liquid air temperatures is appreciable, the pressures read on the manometers were reduced by 0.007 mm. (V.P. of phosphine at the temp. of the liquid air used) Suitable small corrections were also applied to the observed pressure of non-condensable gas, owing to cooling of the side tube in which the phosphine was frozen out. Care was taken that the liquid air was always the same distance up the side tube. Δp is the change in total pressure and ΔPH_3 the decrease in phosphine pressure, calculated from the manometer readings. Unfortunately the analysis of the hydrogen oxygen mixtures was not very accurate, as, after compressing into the combustion bulb, the total pressure was only about 10mm; the results are probably only accurate to about 10%.

Had the reaction proceeded according to the equation $PH_3 + O_2 \rightarrow H_2 + HPO_2$, then the pressure of non-condensable gas should have remained constant, whereas, as can be seen from Table IX, the pressure increases to about double its original value when the oxygen pressure is one fourth that of phosphine (Experiments 181 - 184). In experiments 176--179, where the oxygen pressure is one half that of phosphine, $p_{N.C.}$ does not increase so quickly, and finally, when $O_2 : PH_3 :: 2 : 1$, N.C. actually decreases. In the first case then, there must be some decomposition of the phosphine accompanying the oxidation, and in the last case part of the hydrogen will probably be oxidised to water. These conclusions are supported by the hydrogen oxygen analyses, for in Experiments 181 - 184 the value of pH_2 increases during the course of the reaction, but in Experiments 186 - 189, i.e., with O_2 high, although pO_2 steadily falls, there is no corresponding increase in pH_2. It is evident that the change in total pressure (Δp) cannot be used as a measure of the reaction rate. This can best be seen in Experiments 181-184, where Δp remains almost constant after two minutes, although the change in the phosphine pressure shows that the reaction is still proceeding.

The best measure of the rate of reaction would appear to be the change in phosphine pressure, with the reservation that in comparing the rates with different proportions of oxygen and phosphine, the initial rate would probably give better results than determining the time required for a definite fraction of the phosphine to react.

For comparison with Table IX, a similar series of experiments using a tungsten filament are given in Table X.

Essentially similar results were obtained with the tungsten filament. Even with a 1:1 mixture, there is no very close correspondence between Δp, ΔPH_3, and

TABLE X.

Temperature of filament 768.
Dimensions as in Table IX.

Expt. No.	Reaction Time.	PH_3	O_2	Final press.		NC	PH_3	H_2	O_2
232	2	0.397	0.401	0.734	0.064	0.382	0.045	0.047	0.335
233	4	0.405	0.401	0.709	0.097	0.367	0.063	0.075	0.292
234	8	0.403	0.400	0.591	0.212	0.358	0.170	0.132	0.226
235	2	0.397	0.159	0.535	0.021	0.167	0.029	0.032	0.135
236	4	0.402	0.160	0.530	0.032	0.168	0.040	0.081	0.087
237	8	0.397	0.159	0.499	0.055	0.184	0.080	0.122	0.061
238	2	0.411	0.747	1.087	0.071	0.742	0.066	0.114	0.628
239	4	0.409	0.743	1.003	0.149	0.720	0.126	0.176	0.543
240	8	0.407	0.745	0.955	0.198	0.706	0.158	0.237	0.469

TABLE XI

Same experimental conditions, Mo filament.

	PH_3	0.425)	172	0.403)	191		0.403)	185
	O_2	0.406)		0.095)			-)	
Time (mins.)	Total press.	PH_3	PH_3		PH_3	PH_3	PH_3	
0	0.831	0.425	0	0.498	0.403	-	0.020	
1	0.702	0.336	0.089	0.488	0.373	0.030	0.020	
2	0.635	0.283	0.142	0.476	0.349	0.054	0.028	
4	0.574	0.224	0.201	0.466	0.310	0.093	0.061	
8	0.515	0.151	0.274	0.464	0.265	0.138	0.137	

p_{H_2}, which would be the case if H_2 and HPO_2 were the only products. In subsequent experiments to determine the kinetics of the reaction, analysis of the mixture was affected at certain time intervals by condensing out the phosphine in the side tube by means of liquid air, and measuring the residual pressure of the gas. After this the side tube was heated up to room temperature, and a short time (5 min.) allowed for the gases to mix completely before again switching on the current in the filament. Corrections had, of course, to be applied to the $p_{N.C.}$, owing to the vapour pressure of phosphine at liquid air temperatures, and to the cooling of the side tube.

In Table IX the pressure of phosphine remained constant and that of oxygen was varied; in Table XI some additional results are recorded, as well as a decomposition run in order to find by how much the rate of oxidation was faster than the rate of decomposition. (Table XI is on page 59.)

Table XII gives a number of experiments in which the initial pressure was kept constant and phosphine pressure varied.

TABLE XII.

Same experimental conditions.

Exper.	Total press.	Δp	p_{NC}	p_{PH_3}	Δp_{PH_3}	Time.
204	0.490	--	0.376	0.114		0
	0.432	0.058	0.348	0.084	0.030	1
	0.397	0.093	0.339	0.058	0.066	2
	0.350	0.140	0.316	0.034	0.080	4
	0.326	0.164	0.305	0.021	0.093	8

Experiment 205.

Time	Total Press.	Δp	p_{NC}	p_{PH_3}	Δp_{PH_3}
0	0.576	--	0.376	0.200	--
1	0.451	0.125	0.346	0.105	0.095
2	0.384	6.192	0.327	0.057	0.143
4	0.331	0.245	0.314	0.017	0.183
8			0.305		

Experiment 206.

Time	Total Press.	Δp	p_{NC}	p_{PH_3}	Δp_{PH_3}
0	1.154	--	0.372	0.782	--
1	1.099	0.055	0.395	0.704	0.078
2	1.050	0.104	0.397	0.653	0.129
4	1.005	0.149	0.433	0.572	0.210
8	0.961	0.193	0.493	0.468	0.314

Experiment 207.

Time	Total Press.	Δp	p_{NC}	p_{PH_3}	Δp_{PH_3}
0	0.768	--	0.371	0.397	--
1	0.653	0.115	0.355	0.298	0.099
2	0.596	0.172	0.352	0.244	0.153
4	0.543	0.225	0.354	0.189	0.208
8	0.495	0.273	0.363	0.139	0.265

These data are plotted in figs. 7 & 8 . In the former, the initial rate (R), the initial minus the rate of decomposition of the phosphine and the quantity $1/T - 1/T_0$ (T is the time required for Δp PH_3 to reach 0.1mm., and T_0 that for decomposition of phosphine) are plotted against the oxygen pressure. The three methods of plotting the results give closely parallel results, and it may be concluded that the order with respect to oxygen pressure is two, since on plotting $1/T - 1/T_0$ against $(O_2)^2$, the line obtained is straight (Fig.7). Inspection of Fig (8), where Δp PH_3 is plotted against time for three different pressures of phosphine shows that the order of the reaction is nearly zero. It was unfortunately impossible to extend the experiments to higher pressures owing to the intervention of explosion.

During these experiments, it was observed that a fai faint glow accompanied their progress. There was thus an indication of part of the action being homogeneous. In Table XIII, therefore, three runs are given, using the same pressures of phosphine and oxygen; in experiment 201, argon was present at the start; in 202, argon was added after three minutes reaction, and 203 is a run without argon. In all cases, as the decrease in phosphine pressure shows, there is no change in rate, and therefore an appreciable portion of the present reaction cannot be a chain process, since argon does accelerate the photo-chemical oxidation below the lower limit. (Melville P.R.S. 1932 A, 138, 389).

TABLE XIII.

Mo filament, temp. 836 K.

		202.
201. PH_3	0.409	0.424
O_2	0.380	0.375
A	0.512	0.603

Time.	p_{Total}	p PH_3	Δ PH_3	p_{total} ~~PH_3~~ *	p PH_3	Δp PH_3
0	1.301	0.409	-	0.799	0.424	-
1	1.204	0.303	0.106	0.689	0.327	0.097
2	1.127	0.252	0.157	0.635	0.277	0.147
3	--	-	-	0.606	0.248	0.176
4	1.082	0.208	0.201	0.588	0.201	0.214
5	-	-	-	0.566	0.203	0.231
7	-	-	-	0.547	0.169	0.255
8	1.033	0.158	0.251	-	-	-

* p_{total} does not include the pressure of the argon.

<u>203.</u>

T

p_{PH_3} 0.424
p_{O_2} 0.375

Time		-	
		PH_3	PH_3
0	0.799	0.424	-
1	0.693	0.330	0.094
2	0.632	0.274	0.150
3	0.596	0.241	0.183
4	0.579	0.220	0.204
5	0.563	0.199	0.225
7	0.547	0.178	0.246
8	-	-	-

Experiments were also made at total pressures of the order of 0.1 mm., but again no acceleration by inert gas could be observed. The homogeneous reaction which is responsible for the appearance of the glow must thus be only form a very small part of the total reaction. This is consistent with the fact that the intensity of the glow is even less than in the oxidation of phosphorus, where the rate of oxidation was about 0.1 of that obtaining in the present experiments.

<u>Temperature Coefficient</u>. This was measured in a straightforward manner: in order to ensure an accurate comparison, the apparent energies of activation of the oxidation and decomposition were measured with the same specimen of wire, the one immediately after the other.

(See next page for Table XIV.)

<u>Tungsten Filament</u>. The above results have shown that oxygen does not displace adsorbed phosphine from a molybdenum filament, since the rate of reaction is almost independent of PH_3, thus agreeing with the data

TABLE XIV.

No.	PH_3	O_2	Temp K	$\log_{10}T/4$	$\log_{10}T/2$	E
286	0.412	0.426	720	1.699	-	35.8
285	0.426	0.416	691	0.230	-	
284	0.424	0.402	665	0.591	-	
287	0.417	0.439	651	0.699	-	
288	0.420	-	878	-	0.231	23.8
289	"	-	836	-	0.505	
290	"	-	793	-	0.820	
291	"	-	758	-	1.159	

T/4 is the time for 25% reaction, i.e. for the consumption of 25% of the PH_3: T/2 is that for the decomposition of 50% of the PH_3.

on the decomposition. With tungsten , however, the decomposition at pressures of the order of 1 mm. is unimolecular, and therefore it might be expected that the total order of the reaction would be two if the oxygen is not strongly adsorbed. The variation of the rate with $p\mathrm{PH_3}$ and $p\mathrm{O_2}$ is given by the data in Table XV; the method of gas analysis and general procedure were exactly the same as that adopted with molybdenum, including the glowing of the filament between the runs in order to obtain reproducible results.

TABLE XV.

Tungsten filament, temperature 768°K.

Experiment 221.

PH_3 0.404
O_2 0.411

Time	p	Δp	$p\,PH_3$	$\Delta p\,PH_3$
0	0.815	-	0.404	-
1	0.780	0.035	0.381	0.023
2	0.739	0.076	0.352	0.052
4	0.689	0.126	0.323	0.081
8	0.617	0.198	0.272	0.132

Experiment 222.

PH_3 0.403
O_2 0.245

0	0.648	-	0.403	-
1	0.626	0.022	0.388	0.015
2	0.603	0.045	0.367	0.036
4	0.569	0.079	0.337	0.066
8	0.526	0.122	0.297	0.106

Experiment 223.

PH_3 0.403
O_2 0.412

0	0.487	-	0.403	-
1	-	-	-	-
2	0.477	0.010	0.883	0.020
4	0.470	0.017	0.363	0.040
8	0.461	0.026	0.333	0.070

Experiment 224 **Experiment 225.**

Experiment 224: PH_3 0.413; O_2 0.819

Experiment 225: PH_3 0.420; O_2 -

Time	p	Δp	$p\,PH_3$	$\Delta p\,PH_3$	$p\,PH_3$	$\Delta p\,PH_3$
0	1.232	-	0.413	-	0.420	-
1	1.163	0.069	0.371	0.042	-	-
2	-	-	-	-	0.407	0.013
4	1.020	0.212	0.269	0.144	0.398	0.022
8	0.892	0.340	0.184	0.229	0.368	0.052

Experiment 227. PH_3 0.127; O_2 0.412

0	0.539	-	0.127	-
1	-	-	-	-
2	0.282	0.056	0.101	0.026
4	0.449	0.090	0.081	-
8	0.398	0.141	0.051	0.076

Experiment 228.

PH_3 0.262
O_2 0.411

0	0.673	-	0.262	-
1	0.636	0.037	0.254	0.008
2	0.607	0.066	0.223	0.039
4	0.564	0.107	0.190	0.072
8	0.506	0.167	0.147	0.115

Experiment 230.

PH_3 0.812
O_2 0.398

0	1.210	-	0.812	-
1	1.190	0.020	0.786	0.026
2	1.159	0.051	0.737	0.075
4	1.123	0.087	0.712	0.100
8	1.061	0.149	0.649	0.163

The data of Table XV are plotted in fig. 10 Curve 1. represents $R - p\,O_2$ and curve $2, (R + R_o) - O_2$ plotted against oxygen pressures, R_o being the rate of decomposition of phosphine. The rate is seen to be nearly proportional to the oxygen pressure in the case of a tungsten filament compared with the bimolecular course found for molybdenum. Curve 3. is for varying phosphine pressures and here the order is less than unity since the initial increase in R is not maintained, but gradually falls off. If log R be plotted against log $p\,PH_3$, the slope of the line obtained is 0.5 and therefore $R \propto p\,PH_3^{\frac{1}{2}}$. (~~Fig.~~)

The effect of argon was also investigated to see if there was any measurable chain reaction, as a faint glow was observed in these experiments. Again, however, no acceleration could be detected so that the reaction must occur almost entirely on the surface of the filament. A run was also done with hydrogen present at the start to see if any hydrogen formed during the reaction could alter its course. These results are given in Table XVI.

No. 251

TABLE XVI.

PH_3 0.399
O_2 0.397
A 0.514

Time	Total p.	Δp	p N.C.	$p\,PH_3$	$\Delta p\,PH_3$
0	1.310		0.911	0.399	
1	1.291	0.019	0.927	0.366	0.035
2	1.272	0.038	0.920	0.352	0.047
4	1.240	0.070	0.914	0.326	0.073
8	1.184	0.126	0.908	0.276	0.123

No. 252 PH_3 0.395
O_2 0.387
H_2 0.484

0	1.266		0.871	0.395	
1	1.234	0.032	0.864	0.370	0.025
2	1.199	0,067	0.847	0.352	0.043
4	1.152	0.114	0.850	0.302	0.093
8	1.084	0.180	0.845	0.239	0.156

No. 241.

PH_3 0.397
O_2 0.391

Time.	Total p.	Δp	p N.C.	p PH_3	Δp PH_3
0	0.788		0.391	0.397	
1	0.755	0.033	0.384	0.371	0.026
2	0.726	0.062	0.375	0.351	0.046
4	0.672	0.116	0.370	0.302	0.095
8	0.592	0.196	0.362	0.230	0.167

Temperature Coefficient.

In Table XVII data are given for the oxidation and decomposition at a number of different temperatures. It will be observed that although the rate of oxidation is not much faster than the rate of decomposition, yet the fact that the pressure of noncondensable gas decreases a little shows quite definitely that there is very little decomposition accompanying the oxidation.

TABLE XVII.

For decomposition results see Table VII.

Oxidation.

No. 241.

Time.	Total p.	Δp	p N.C.	p PH_3	Δp PH_3	Tempr.
0	0.788		0.391	0.397		
1	0.755	0.033	0.384	0.371	0.026	
2	0.726	0.062	0.375	0.351	0.046	495°C.
4	0.672	0.116	0.370	0.302	0.095	
8	0.592	0.196	0.362	0.230	0.167	

No. 242.

0	0.795		0.396	0.399		
1	0.716	0.079	0.384	0.332	0.067	
2	0.659	0.136	0.380	0.279	0.120	560°C.
4	0.576	0.219	0.375	0.201	0.198	
8	0.467	0.328	0.375	0.092	0.307	

No. 243

Time.	Total p.	Δp	p N.C.	p PH_3	Δp PH_3	Tempr.
0	0.794		0.395	0.399		606 °C
1	0.699	0.095	0.389	0.310	0.089	
2	0.621	0.173	0.382	0.239	0.160	
4	0.527	0.267	0.374	0.153	0.246	
No. 244						
0	0.795		0.394	0.401		425 °C
2	0.774	0.021	0.392	0.382	0.019	
4	0.756	0.039	0.385	0.371	0.030	
8	0.731	0.064	0.374	0.357	0.044	
16	0.690	0.105	0.365	0.325	0.076	
No. 245						
0	0.804		0.392	0.412		457 °C
2	0.775	0.029	0.374	0.401	0.011	
4	0.749	0.055	0.360	0.381	0.031	
8	0.712	0.092	0.360	0.352	0.060	
16	0.657	0.147	0.347	0.310	0.102	

From these results $E_{oxid.} = 21.8$ Kg.cal.

As the purpose of this work was to investigate certain chain phenomena, two further efforts were made to induce the initiation of chains. A silica and also a pyrex filament replaced the tungsten one, but although the rate of oxidation was greater than that of the decomposition, no acceleration by argon was observed. The pyrex filament was made by drawing down pyrex tubing to a fine spindle and inserting tungsten wire through the bore. To prevent reaction occurring on the tungsten surface, the wire was spot-welded to nickel leads and the ends of the pyrex tube filled in with lead.

Finally, owing to the fact that phosphine raises the lower oxidation limit of $P_4 - O_2$ mixtures,[39] Phosphorus vapour was added to phosphine oxygen mixtures in the hope that since a reaction occurs on the surface which leads to the evaporation of a molecule capable of starting the $P_4 - O_2$ chains, the same molecule might provide centres for phosphine reaction. There was, however, no acceleration of the reaction, indeed a slight retardation was found. The pressure of phosphorus vapour did not exceed 0.03 mm.

A peculiar observation with regard to the deposition of red phosphorus was made after a number of oxidations experiments had been carried out. The walls of the reaction tube opposite the hot portion of the filament were covered by a fairly uniform layer of HPO_2. When phosphine was decomposed on the filament, the red phosphorus was not deposited on top of the acid film, but at the extreme ends of the tube where there was little HPO_2. The phosphorus molecules (P_2, as suggested previously) are apparently efficiently reflected from an HPO_2 surface, but are relatively easily condensable on a silica surface.

DISCUSSION.

It is seen from the foregoing results that the orders of the decomposition and oxidation of phosphine on molybdenum, with respect to the phosphine pressure, are nearly the same in the pressure region where comparison may be made. It would then appear that oxygen cannot displace adsorbed phosphine under these conditions. Oxidation then probably occurs by the impact of molecular oxygen on a phosphine-covered filament. When the oxygen pressure is equal to or less than that of the phosphine, and where analysis of the gas mixtures shows that HPO_2 is being produced, the simplest mechanism which can be postulated is the following. Phosphine is decomposed, step by step, on the molybdenum surface: $Mo - PH_3 \rightarrow Mo + PH_2 \rightarrow Mo + PH \rightarrow Mo + P$, the PH_2, PH or P remaining strongly adsorbed until there is reaction between adjacent radicals to yield phosphorus and hydrogen which evaporate. During the progress of this series of reactions andoxygen molecule may collide with a PH radical to form HPO_2. If the oxygen pressure is very small, the probability of reaction is so small that most of the PH_3 is decomposed directly into its elements. On the other hand, if p_{O_2} is large, the phosphine would seem to be attacked before the intermediate steps in its decomposition take place, for the decrease in pressure of non-condensable gas points to the production of a highly oxidised molecule, such as H_3PO_4. It may be that it will then be necessary for two oxygen molecules to collide in close proximity to one PH_3 molecule, in order to effect this oxidation, inwwhich case the reason for the bimolecular nature of oxidation would become clear. Why the reaction should follow a bimolecular course when only HPO_2 is formed is not however obvious.

A somewhat similar mechanism would also apply to the reaction on tungsten filaments. In this case there are deviations. For example, the order of the reaction with respect to phosphine pressure is not unity as in the decomposition experiments. This is possibly due to the fact that since phosphine is not so strongly adsorbed on tungsten as on molybdenum, oxygen is able to hinder the increased degree of adsorption necessary to maintain unimolecular characteristics. With tungsten, therefore, the oxidation probably occurs by the interaction of adsorbed phosphine or its intermediate products of dissociation and oxygen on the metal surface.

In spite of these two slightly different methods of oxidation the possibility of the evaporation of a molecule capable of starting a chain in the gas phase must be very small. Even when $p\mathrm{O}_2$ is much less than $p\mathrm{PH}_3$, and there is a chance of the evaporation of P_2 molecules, there is no homogeneous reaction. The experiments with phosphorus vapour likewise indicate that the carriers in the phosphorus oxygen reaction cannot induce reaction in phosphine-oxygen mixtures. In this case, of course, the ejection of carriers from the filament may be interfered with by phosphine itself. Some such action is not altogether unexpected in view of the fact that phosphine has the unique property of raising the lower explosion limit of phosphorus vapour. Another point emerges from these experiments: HPO_2 molecules when evaporated from a hot filament are incapable of reacting with oxygen to yield suitable chain carriers. The difference in the phosphine and phosphorus reactions must therefore be due to the behaviour of these molecules on the surface of the catalyst. In the former the interdediate products of dissociation, which are undoubtedly reactive and suitable for chain propagation, as is shown by the photo-chemical experiments, are so strongly adsorbed at the metal surface that they are unable to evaporate before attack by oxygen. The faint glow that is observed may be due to a very small fraction of these being ~~un~~able to escape from the surface before oxidation and set in train chains in the gas. In the phosphorus reaction, on the other hand, the only intermediate product is probably P_2 (the filament is hardly hot enough for P atoms to be present in any quantity, cf. Preuner and Brockmoller[35]), which can be easily and quickly desorbed from the surface before the arrival of O_2 molecules. On a platinum filament, where the reaction takes place wholly on the surface, the fact that the rate is of zero order with respect to phosphorus concentration, shows that adsorption is very strong. An O_2 molecule has therefore a good opportunity of reacting with adsorbed phosphorus.

It has been shown (Fig.10) that the rate of oxidation on molybdenum is somewhat faster than the decomposition at 836°K. If, however, the velocity measurements could be extended to a much wider range, it would be observed, since E_O is greater than E_D, (a) at temperatures higher than 836°K, the rate of oxidation would become very much greater than that of the decomposition; (b) at temperatures less than 836°K, the decomposition would become the preponderant reaction and the oxygen would be without influence. These effects would not be noticed with the tungsten filament as it is a remarkable fact that $E_O = E_D$.

PART II.

In the first part of this thesis experiments are described, in which efforts were made to find if the kinetics of the chain reaction between phosphine and oxygen could be investigated by means of hot tungsten and molybdenum filaments, just as in the phosphorus-oxygen reaction.[37.] Now, it has been shown that, under the conditions employed, the oxidation of phosphine is almost entirely a surface reaction, and so other means must be employed for investigation of the problems cited in the introduction to Part I. Failing the filament method, the most suitable means to adopt are:

1. The Photosensitised reaction, using excited (2^3P_1) mercury atom.

2. The direct photo-reaction caused by a zinc spark.

The suitability of these two methods for the present investigation has been pointed out by Melville.[31.32.]

The kinetics of the phosphine-oxygen reaction have been worked out by Dalton and Hinshelwood,[7.] Dalton and Melville,[31.32.] and a theory of chain reactions suitable to both the stable and explosive reactions has been developed. It will not be out of place to give a summary of the theory here.

Consider the reaction taking place in the following stages:

1. A process by which the chain carrier X_p is formed. Let this rate be E.(c). Assume for the

present that only X_p is formed spontaneously.

2. $O_2 + X_p \rightarrow X_o$ ...... velocity coefft.= k_2
3. $X_o + PH_3 \rightarrow X_p$ ...... " " = k_3
4. Deactivation of X_o " " = K
5. Deactivation of X_p " " = K

X_o is the chain carrier derived from the oxygen molecule. This is assumed by Semenoff[8] to be an oxygen atom. X_p is the carrier whose origin is due to reaction between phosphine and X_o. Then:

$$\frac{d[X_p]}{dt} = F(c) + k_3[Xo][PH_3] - k_2[Xp][O_2] - K[Xp] = 0 \quad (1)$$

It is here assumed that deactivation of Xp occurs at the walls of reaction tube, i.e., that the reaction is taking place at low pressure. Also:

$$\frac{d[Xo]}{dt} = k_2[Xp][O_2] - k_3[Xo][PH_3] - K[Xo] = 0 \quad (2)$$

It is assumed that both the chain propagators, Xo and Xp are equally easily destroyed at the walls. If one carrier were more easily destroyed than the other, the lower exp. limit would be:

$$[PH_3]\left\{[PH_3] + [O_2]\right\} = \text{constant.}$$

or

$$[O_2]\left\{[PH_3] + [O_2]\right\} = \text{constant}$$

which is not in so good agreement with the experiment as that given later.

therefore: $F(c) = K\left\{[Xo] + [Xp]\right\}$

$$[Xp] = \frac{F(c)}{K} - [Xo]$$

therefore: $$[Xo] = \frac{F(c)K + k_2[O_2]F(c)}{K^2 + k_3[PH_3]K + k_2K[O_2]}$$

Now, if the chain length is great $F(c)K$ can be neglected in comparison with $k_2[O_2]F(c)$; also K^2 can be left out of the denominator of the expression.

Therefore: $$[Xo] = \frac{k_2[O_2]F(c)}{k_3[PH_3]K + k_2K[O_2]}$$

Let $K' = K\left\{[PH_3] + [O_2] + [A]\right\}$, i.e. K' expresses the efficiency of deactivating collision with the walls. ($[A]$ is concentration of inert gas). Also let $k_2 = k_3$. This is fairly well justified, cf. Dalton and Hinshelwood,[48.] also Melville.[31.]

Therefore $[Xo] = \frac{[O_2]F(c)}{K'}$ if $[A] = 0$.

Now if I is the intensity of the light absorbed,

$$F(c) = \frac{I[PH_3]}{[PH_3] + 0.5[O_2] + 0.37}$$

The term $[PH_3]$ in the numerator allows for the formation of Xp radicals by means of the reaction $Hg' + PH_3 \rightarrow Xp$ ... and the phosphine and oxygen terms in the denominator represent deactivation of the excited mercury atoms without such a deactivating collision being effective in forming a chain carrier. In this respect PH_3 is twice as effective as oxygen. The excited Hg' atom can also lose its energy by reradiation of light absorbed. This fact is taken account of by putting in the term 0.37 in the denominator.

Then for the photo-sensitised reaction,

$$-\frac{d[PH_3]}{dt} = \text{Rate} = k_3[PH_3][Xo]$$
$$= \frac{k_3[PH_3][O_2]F(c)}{K'}$$

$$= \frac{k_3 [PH_3]^2 [O_2] I}{K' \left\{ [PH_3] + 0.5 [O_2] + 0.37 \right\}} \qquad (3)$$

and for direct photochemical reaction,

$$- \frac{d [PH_3]}{dt} = \frac{k_3 [O_2] [PH_3]^2 I}{K'} \qquad (4)$$

Explosion limits.

It has been assumed in the theory of the stable reaction given above, that when the radicals Xp and O_2 (or X_o and PH_3) react, there is exactly one Xo (or Xp) radical produced. Now this need not necessarily be the case, so, as in the introduction, Part I, let α be the average number of Xo radicals produced in a collision between Xp and an oxygen molecule, effective in deactivating the Xp radical. If α is less than one, the velocity of reaction can only be great if deactivation by the gas and the walls are small. When, however, α becomes greater than unity, explosive reactions may take place as was suggested by Semenoff.[8.] If a reaction is sufficiently exothermic this condition may become possible. The kinetic equations now become:-

$$\frac{d[Xo]}{dt} = k_2 [Xp][O_2] - k_3 [Xo][PH_3] - K[Xo] = 0 \qquad (5)$$

$$\frac{d[Xp]}{dt} = F(c) \; k_3 [Xo][PH_3] - k_2 [Xp][O_2] - K[Xp] = 0 \qquad (6)$$

solving for Xo :-

$$[Xo] = \frac{k_2 [O_2] F(c) + K F(c)}{(1 - \alpha) k_2 k_3 [PH_3][O_2] + k_2 K [O_2] + k_3 K [PH_3] + K^2} \qquad (7)$$

Now, if α is greater than one the first term in the denominator of (7) becomes negative and if the negative value is large enough it may become greater than the deactivation terms $k_2K[O_2] + k_3K[PH_3] + K^2$. This means that on account of the branching of the chains taking place, the number of new chains starting in any given time is greater than the number terminated; so no stationary condition is possible and explosion takes place. At the concentrations of phosphine and oxygens which make the denominator of (7) equal to zero, there is a critical explosion limit. This limit may be very sharp, on one side the rate of reaction may be very small or even negligible, while on the other side it is infinitely rapid. It is seen from the above theory that the rate of starting of the chains $F(c)$ should have no effect on the value of the critical limit. On the other hand $F(c)$ cannot be zero or this theory of explosion limits falls to the ground. It appears then that $F(c)$ must have a certain minimum value below which no explosion can take place.

The critical limit may be either a lower limit or an upper limit: this comes about in the following way. Chains are broken either in the gas phase or at the walls. Now, at low pressures the chains will be able to get to the walls easily and be destroyed there, whereas at increased pressures this wall deactivation ~~will~~ become less and ultimately explosion will take place. On increasing the gas pressure still further, it is conceivable that the controlling factor in the destruction of chain centres is deactivation by the gas, and thus increase of pressure aids deactivation and so a steady state is again obtained.

This transition from slow reaction to vigorous - explosion is adequately explained by the branching chain theory. It is possible, however, that the explanation of these transitions is not the same in every case. It has been suggested that in certain reactions a critical limit may occur in other ways.[52.]

1. In the reaction between hydrogen and oxygen in presence of small quantities of nitrogen peroxide, it has been found[51.] that the union is explosive if the pressure of nitrogen peroxide lies between two sharply defined limits. This has been explained in the following way:- It is suggested that a surface reaction involving the nitrogen peroxide is responsible. At low pressures the nitrogen peroxide favours the surface reaction owing to its mass action effect, whilst at high pressures this surface reaction is inhibited by the nitrogen peroxide displacing the other reactant from the surface. When the surface reaction is near its maximum value there may be enough energy generated on the surface to start explosion. This explanation has been dropped, as far as this reaction is concerned, in favour of Semenoff's branching theory.

2. Alyea[14.] has pointed out a way in which an upper limit might originate. He suggests that in mixtures of hydrogen and oxygen above the upper limit a layer of hydrogen covers the walls of the reaction vessel,

preventing departure from it of chains which would branch and give rise to explosion in the gas. As the pressure is reduced, a point is reached at which this hydrogen is suddenly stripped from the wall by oxygen, and it is now possible for chains to leave the surface. In principle the mechanism is a possible one, but its applicability to this reaction is doubtful.[53]

3. In the case of mixtures of cyanogen and oxygen an explanation of the lower limit has been put forward by Hadow and Hinshelwood.[54] If there is a finite rate of adsorption of the different gases admitted to the reaction bulb, and if the two gases compete for the possession of the surface, then the relative amounts of the two gases adsorbed immediately on admission may not be the same as that a few instants later. The rate of reaction between the two gases may at the first instant, then,,be different from the rate a moment later: or, specially, it may be much greater. If, now, this momentary rate becomes rapid enough to inflame the gas as a whole, there will be the appearance of explosion limits.

It has been shown that in the case of the phosphine oxygen reaction, the theory that explains the greater part of the observed phenomena is that of the branching chain mechanism.

In equation (7) is given the value of the concentration of Xo radicals. Now, in order that this value should increase indefinitely, the denominator of the right hand side of the equation must be equal to zero. Then, making simplifications as before:-

$$(\alpha - 1)k_3[PH_3][O_2] = K\left\{[O_2] + [PH_3]\right\} \qquad (8)$$

or $$(\alpha - 1)k_3[PH_3][O_2] = K' \qquad (9)$$

or $p_{PH_3} \times p_{O_2}$ = constant.

This value for the explosion limit agrees over a certain range with that obtained experimentally.[48] Outside this range, deviations occur, due to deactivation occurring partially in the gas phase, when the pressure of one gas is much greater than that of the other.

Now, if inert gas such as argon or nitrogen is added to the reaction mixture, the value of K' will now be $K\left\{[O_2] + [PH_3] + [A]\right\}$, where $[A]$ is concentration of inert gas. Equation (9) now becomes:-

$$(\alpha - 1)k_3[PH_3][O_2] = K'\frac{[O_2] + [PH_3]}{[O_2] + [PH_3] + [A]}$$

$$p_{O_2} \times p_{PH_3}\left(1 + \frac{p_A}{p_{O_2} + p_{PH_3}}\right) = \text{constant for any given tube} \qquad (10)$$

In this equation a factor μ must be introduced to take into account the various speeds and molecular diameters of the inert gas molecules. Equation (9) now becomes:-

$$p_{O_2}p_{PH_3}\left(1 + \frac{\mu\, p_A}{p_{O_2} + p_{PH_3}}\right) = \text{constant for any given tube.} \qquad (11)$$

The value of the upper limit has been worked out by Dalton.[7] In it, it is assumed that no deactivation of chain carriers occurs at the walls, but that deactivation occurs in the gas phase by three body collisions between an Xo carrier, and an oxygen molecule and a third molecule, either oxygen, phosphine, or inert gas. The idea of chains breaking in three body collisions is also proposed by Semenoff in the case of H_2-O_2 reactions. In this case, the last term in equation (5) becomes:-

$$k_6[Xo][O_2]^2 + k_{11}[Xo][O_2][PH_3] + k_{12}[Xo][O_2][A]$$

(k_6, k_{11}, and k_{12} are velocity coefficients).

The assumption that the upper limit is due to deactivation in the gas is fairly well justified, for inert gas, instead of increasing the explosive tendency, as at the lower limit, tends to stop explosion. Increase of tube diameter which assists explosion at the lower limit has no effect on the value of the upper limit.

Equation (5) becomes now:-

$$\frac{d[Xo]}{dt} = k_2[Xp][O_2] - k_3[Xo][PH_3] - k_6[Xo][O_2]^2 = 0$$

It is assumed that there is no inert gas present, and that the oxygen pressure is so much greater than that of phosphine that deactivating collisions of the type $Xo + PH_3 + O_2$ are negligible.

Equation (6) becomes:-

$$\frac{d[Xp]}{dt} = F(c) \quad k_3[Xo][PH_3] + k_2[Xp][O_2] = 0$$

$$\therefore \quad Xp = \frac{k[Xo][O_2]^2 - F(c)}{(\alpha - 1)\, k_2[O_2]}$$

$$Xo = \frac{2F(c) - \alpha F(c)}{(\alpha - 1)k_3[PH_3] - k[O_2]^2}$$

which, on equating the denominator to zero, gives for the value of the upper limit:-

$$(\alpha - 1)k_3[PH_3] = k_6[O_2]^2 \qquad (12)$$

or

$$\frac{[O_2]^2}{[PH_3]} = \text{constant.}$$

provided the PH_3 pressure is not great.

This value is justified experimentally.[7]

A simple method of arriving at the absolute value of k_6 has been put forward by Semenoff.[56]

For the lower limit:

$$(\alpha - 1)k_3[PH_3][O_2] = K' \qquad (15)$$

and the upper limit:

$$(\alpha - 1)\ k_3[PH_3] = k_6[O_2]^2 \qquad (16)$$

Let the pressure of oxygen at the upper and lower limits of two mixtures containing the same amount of phosphine be $[O_2]_2$ and $[O_2]_1$. Then:

$$(\alpha - 1)k_3[PH_3][O_2]_1 = K'$$

$$(\alpha - 1)k_3[PH_3] = k_6[O_2]_2^2$$

$$k_6 = \frac{K'}{[O_2]_2^2 \times [O_2]_1} \qquad (17)$$

K' can easily be found from the lower limit data, and so the value of k_6 is obtained.

It is proposed to study the stable chain reaction at pressures above the upper limit using both the mercury sensitised reaction and the direct photo-chemical reaction.

Equations (1) and (2) must now be altered if conditions at and above the upper limit are to be studied.

$$\frac{d[Xo]}{dt} = F(c) + k_2[Xp][O_2] - k_3[Xo][PH_3] - F(XoQA) = 0 \qquad (13)$$

$$\frac{d[Xp]}{dt} = k_3[Xo][PH_3] - k_3[Xo][O_2] - F(XpOA) = 0 \qquad (14)$$

Now there are six possible ways in which a chain carrier can be destroyed in the gas phase.

These six possibilities are:-

1. The carrier Xo is destroyed in a bimolecular collision with any molecule in the system with which it cannot react to form Xp;

$Xo + X \rightarrow X' +$ coefft. $= k_4$

2. Two Xo radicals are destroyed in a three body collision with a third molecule, either oxygen or inert gas.

$Xo + Xo + X \rightarrow$ coefft. $= k_5$

This method of destruction is unlikely to have much effect on the reaction, as the probability of this type of collision occurring is very small owing to the small value of Xo .

3. An Xo radical is destroyed in a termolecular collision with two other gas molecules.

$Xo + X + X$ coefft. $= k_6$

The molecules X might be either oxygen or inert gas, so there are here three possibilities:

$Xo + A + O_2$

$Xo + O_2 + O_2$

$Xo + A + A$

It might also be possible for phosphine to act as a deactivator in a collision of the type $Xo + PH_3 + O_2$. It is conceivable that this collision could take place without forming an Xp radical.

4. The chain propagator Xp is destroyed in a two body collision.

$Xp + X \rightarrow$ coefft. = k_7

X may be here a PH_3 molecule. This method is unlikely as the pressure of phosphine is small compared with that of oxygen.

5. Two Xps are destroyed in a three body collision of the type :

$Xp + Xp + X$ coefft. = k_8

X may here be a phosphine molecule.

6. An Xp radical is destroyed in a three body collision with two other molecules:

$Xp + X + X$ coefft. = k_9

X is any molecule in the system.

It is possible to work out the dependence of the rate of reaction on phosphine and oxygen concentration, and on the intensity of illumination, assuming that cases 1 - 6 occur exclusively. It is also assumed that $k_2 = k_3$, and in order to simplify the kinetic equations, that PH_3 is negligible when compared with with O_2 . In the experiments the phosphine pressure was about 100 times that of oxygen. Now, as the oxygen pressure is high, it is quite possible that some of the photosensitised reaction may be due to activation of an oxygen molecule by an excited (2^3p_1) Mercury atom. Photosensitised activation is of course also due to dissociation of phosphine molecules by excited mercury atoms. In the direct photo-chemical reaction, however, the light from the zinc spark is absorbed only by the phosphine, and activation by oxygen cannot take place.[32] There is no appreciable absorption of radiation from the zinc spark (by oxygen) - the absorption only begins to be significant at shorter wave lengths.

Then:-

Case 1.

$$\frac{d[Xo]}{dt} = k_2[Xp][O_2] - k_3[Xo][PH_3] - k_4[Xo][O_2] = 0 \qquad (18)$$

$$\frac{d[Xp]}{dt} = F(c) + k_3[Xo][PH_3] - k_2[Xp][O_2] = 0 \qquad (19)$$

$$F(c) = k_4[Xo][O_2] \quad \therefore \quad [Xo] = \frac{F(c)}{k_4[O_2]}$$

$$R = -\frac{d[PH_3]}{dt} = \frac{k[PH_3]}{k[O_2]} . F(c)$$

(a) Initiation caused by phosphine activation alone.

$$R = \frac{k_3[PH_3]}{k_4[O_2]} \cdot \frac{I[PH_3]}{[PH_3] + 0.5[O_2] + 0.37}$$

$$= \frac{k_3[PH_3]^2 I}{0.5k_4[O_2]^2} \quad \text{or} \quad \frac{1}{R} = \frac{[O_2]^2}{[PH_3]^2 I}$$

(b) Initiation caused by oxygen.

$$R = \frac{k_3}{k_4} \frac{[PH_3]}{[O_2]} \cdot \frac{I0.5c[O_2]}{[PH_3] + 0.5[O_2] + 0.37}$$

$$= \frac{k_3[PH_3]I}{k_4[O_2]} \quad \text{or} \quad \frac{1}{R} \quad \frac{[O_2]}{[PH_3]I}$$

(c) Direct Photo-chemical reaction.

$$R = \frac{k_3[PH_3]}{k_4[O_2]} [PH_3] \times I \qquad \text{or} \qquad \frac{1}{R} \propto \frac{[O_2]}{[PH_3]^2 I}$$

It is possible that cases (a) and (b) will have to be combined into an expression of this type:

$$= \frac{k_3 [PH_3]\ I \left\{ [PH_3] + 0.5c[O_2] \right\}}{k_4 [O_2] \left\{ [PH_3] + 0.5 [O_2] + 0.37 \right\}} \qquad (20)$$

in order to allow for activation by both oxygen and phosphine. "c" is a constant denoting the number of chains started per mercury atom deactivated by oxygen.

Case 2.

Now, $\frac{d[Xo]}{dt} = k_2 [Xp][O_2] - k_3 [Xo][PH_3] - k_5 [Xo]^2 [O_2] = 0$

Whence (a)

$$R = \frac{k_3 [PH_3]^{\frac{3}{2}}}{[O_2]} \sqrt{\frac{I}{k_5}}$$

$$\frac{1}{R} \propto \frac{[O_2]}{\sqrt{[PH_3]^3 I}}$$

(b) $$\frac{1}{R} \propto \frac{[O_2]^{\frac{1}{2}}}{[PH_3] I^{\frac{1}{2}}}$$

and (c) $$\frac{1}{R} \propto \sqrt{\frac{[O_2]}{[PH_3]^3 I}}$$

Case 3.

$$\frac{d[Xo]}{dt} = k_2 [Xp][O_2] - k_3 [Xo][PH_3] - k_6 [Xo][O_2]^2 = 0$$

Whence (a)

$$\frac{1}{R} \propto \frac{[O_2]^3}{[PH_3]^2 I}$$

(b) $$\frac{1}{R} \propto \frac{[O_2]^2}{[PH_3] I}$$

and (c) $\frac{1}{R} \propto \frac{[O_2]^2}{[PH_3]^2 I}$.

Case 4.

The corresponding cases for destruction of Xp are obtained in similar ways. The last term in equation (2) is discarded, while the final term of equation (1) becomes (in case 4) $k_7[Xp][PH_3]$.

$$\frac{d[Xp]}{dt} = F(c) + k_3[Xo][PH_3] - k_2[Xp][O_2] - k_7[Xp][PH_3]$$

Whence (a)

$$\frac{1}{R} \propto \frac{1}{I}$$

(b)

$$\frac{1}{R} \propto \frac{[PH_3]}{[O_2]}$$

(c)

$$\frac{1}{R} \propto \frac{1}{[O_2] I_a}$$

Case 5.

$$\frac{d[Xp]}{dt} = F(c) + k_3[Xo][PH_3] - k_2[Xp][O_2] - k_8[Xp]^2[O_2]$$

Whence (a)

$$\frac{1}{R} \propto \sqrt{\frac{1}{I[PH_3]}}$$

(b)

$$\frac{1}{R} \propto \sqrt{\frac{[O_2]}{I}}$$

(c)

$$\frac{1}{R} \propto \sqrt{\frac{1}{[O_2][PH_3] I}}$$

Case 6.

$$\frac{d[Xp]}{dt} = F(c) + k_3[Xo][PH_3] - k_2[Xp][O_2] - k_9[Xp][O_2]^2$$

Whence (a)

$$\frac{1}{R} \propto \frac{[O_2]^2}{I\,[PH_3]}$$

(b) $$\frac{1}{R} \propto \frac{[O_2]}{I}$$

(c) $$\frac{1}{R} \propto \frac{[O_2]}{[PH_3]\,I}$$

There is a possible objection to Case 6., for $Xp + O_2$ is a propagating collision. In presence of a third molecule, however, it is conceivable that a redistribution of energy occurs in such a way as to prevent the emergence of an Xo molecule from the collision.

Up to the present no experiments on the stable phosphine-oxygen reaction above the upper limit have been published, except a few preliminary experiments[57] where a complete quantitative analysis of the problem was not attempted. In this connection the results of Grant and Hinshelwood[58] on the hydrogen oxygen reaction a are noteworthy. The limit here is apparently governed by some form of gas phase deactivation, for argon and helium lower the upper explosion limit. However, above the limit there is a stable reaction which is accelerated by the gases which shows that the chains end on the walls. The explanation given is that the decrease in chain length, as the pressure is reduced, is more than compensated for by the increase in the probability of branching.

EXPERIMENTAL.

The apparatus for this part of the work was similar in form to that used for the filament experiments. A few alterations were however made - see figure 11. The reaction bulb used previously was replaced by a silica test tube, 8" x ¾". This was waxed on to the apparatus with "Picene" wax. To prevent contamination of the pump oil with phosphine, the gases after experiment were pumped out through the liquid air trap T. V. is a stainless steel needle valve, which was used in the explosion limit experiments, to give a means whereby the pressure in the reaction bulb might be reduced. During the other experiments this valve was left open. As the pressures used were sometimes as much as 150 mm., and pressure changes of .002 were being measured, it was found necessary to thermostat the reaction bulb and the oil manometer M_1. The thermostat round the reaction bulb consisted of a metal box with a 6" x 1" silica window let in on one side. This was filled with distilled water. This arrangement was quite satisfactory in keeping the pressure, as read by the oil manometer, constant during the time taken by one run. No heating effect, either by mercury lamp or spark, was observed.

The method of doing a run was as follows:-
The phosphine was admitted to the required pressure as read on the oil manometer, (the measured pressure must be corrected for expansion into the right limb of the

manometer after addition of the oxygen) and condensed out by putting a flask containing liquid air on the reaction tube. The phosphine in the tube leading to the reservoirs was simultaneously condensed back into the reservoir. The tap of M_1 was now opened and oxygen admitted. The apparatus was now allowed to warm up to room temperature and the total pressure measured on the spring gauge (if below 30 mm.) or on the mercury manometer, (if greater than 30 mm.). The tap of M_1 was now shut and the run started, pressure readings being taken at suitable intervals. During the runs the tap to the spring guage was shut, so as to minimise dead space.

Several blank experiments were made with oxygen al alone, to make sure that no spurious results were obtained, for instance, oxygen does dissolve in the oil, but as it was present at the same pressure in both limbs and the time of runs was short, no appreciable change in oil level could be observed. The deposition of phosphoric acid on the walls of the reaction vessel did not cut down the reaction rate for cleaning of the tube had no effect. At the pressures of oxygen used i in these experimens, the phosphine is oxidised completely to H_3PO_4, as is shown by the total pressure decrease being nearly three times the original pressure of the phosphine.

The sources of illumination were:-

Mercury Lamp. The mercury lamp used was of the tungsten anode type with a water cooled mercury cathode. The central portion of the lamp was not cooled, so the surface of the silica did not become covered with mercury, yet the vapour pressure was kept down by the cooling of the cathode. The lamp ran on 4¾ amps. at about 50volts.

The intensity of the lamp was altered by means of the carbon tetrachloride-hexane filter described by Melville and Walls.[50] This varied the incident light, but as practically all the 253.7 radiation is absorbed by a layer of mercury vapour, 3mm thick, pressure 0.001mm the light absorbed is in proportion to the incident light.

<u>Zinc Spark</u>. A rotating form of spark gap was used. This was built on the lines of that described by Holländer and Foerst.[49] The spark was fed from the secondaries of two transformers in parallel. The step up ratio was 100:1. The primary current was 10 amp. and the voltage 50. Condensers of a total capacity of 0.05μF were in parallel with the spark. A strong blast of air steadied the spark and cooled the electrodes.

<u>Explosion limit experiments</u>. Mixtures of phosphine and oxygen were made up as described above, and the total pressure measured. The mixture was then slowly pumped out through the steel needle valve and liquid air trap. The manometer was constantly watched during reduction in pressure, and the pressure just before explosion read. The pressure of each gas at explosion

was calculated by simple proportion. This is justified as the densities and viscosities of phosphine and oxygen are approximately the same, and the two gases will be removed at a rate in proportion to their partial pressures.

RESULTS.

Photo-sensitised oxidation.

It is seen from an inspection of the equations, cases 2 and 5, that the reaction rate should vary as the square root of the intensity, while in the other cases, the reaction is linear. Several possibilities can at once be eliminated if the intensity is first of all investigated. Experiments on the effect of intensity were also done below the lower limit. In this case, in accordance with expectation, the rate was proportional to the light intensity. The results are given in Table XIX, and show quite definitely that for the reaction both above the upper limit and below the lower limit, the rate is proportional to the first power of the intensity. Thus, for the upper limit, cases 2 and 5 are eliminated.

TABLE XIX.

Effect of Intensity. 1. Below the lower limit.

$PH_3 = 0.254$ mm: $O_2 = 0.584$ mm.

Intensity	Init. Rate mm. per min.	$\frac{R}{I}$ *	Time for = 0.0525mm.
1.00	0.072	0.072	0.085
0.15	0.012	0.072	5.20
0.68	0.053	0.072	1.05
0.38	0.028	0.065	2.00
1.00	0.083	0.072	0.70

* Corrected for drift due to change in lamp intensity.

2. Above upper limit.

PH_3 = 0.127 mm. O_2 = 10.0 mm.

Intensity	Time for $\Delta\rho$ = 0.064 mm.	t x I
0.38	1.65	0.63
0.68	0.90	0.61
1.00	0.55	0.55
0.15	3.70	0.56
0.51	1.24	0.63

In Table XX are given a series of experiments in which the intensity of light and the phosphine pressure remained constant whilst that of oxygen was varied. The constancy of the values of R x $[O_2]^2$ shows that the rate is proportional to the inverse of the square of the oxygen pressure.

TABLE XX.

PH_3	0.261	0.261	0.260	0.261	0.261
O_2	20.0	44.0	34.0	27.0	21.4
t.	$\Delta\rho$	$\Delta\rho$	$\Delta\rho$	$\Delta\rho$	$\Delta\rho$
0	-	-	-	-	-
0.25	0.017	0.001	-	0.009	0.016
0.5	0.033	-	0.012	0.021	0.029
0.75	-	-	0.017	0.029	0.043
1.00	0.066	-	0.025	0.041	0.055
1.50	0.092	0.016	0.042	0.056	0.079
2.00	0.098	0.026	0.047	0.073	0.097
3.00	0.162	0.035	0.071	0.104	-
4.00	-	0.055	0.094	-	-
R	0.072	0.013	0.026	0.039	0.063
R x O_2	28.8	25.2	30.0	26.4	28.9

Another series of experiments is given in Table XXI, in which the light intensity and the oxygen pressure were constant, while the phosphine pressure was varied. The constancy of R/ρ_{PH_3} and t x PH_3 shows that the rate is proportional to the phosphine pressure.

TABLE XXI.

Effect of varying phosphine pressure.

PH_3	0.260	0.190	0.129	0.120	0.066
O_2	9.4	10.5	9.2	10.0	10.0
t.	Δp	Δp	Δp	Δp	Δp
0.25	0.024	0.016	0.013	0.012	0.005
0.50	0.050	0.030	0.026	0.020	0.013
0.75	0.075	0.046	0.035	0.030	0.018
1.00	0.096	0.059	0.043	0.039	0.028
1.50	0.134	0.081	0.064	0.055	0.041
2.00	0.166	0.105	0.079	0.069	0.049
3.00	-	0.134	0.100	0.095	0.067
4.00	-	0.160	-	0.116	0.083
R *	0.100	0.066	0.051	0.046	0.025
R/p_{PH_3}	0.385	0.348	0.395	0.384	0.380
t. *	0.65	1.15	1.55	1.86	2.95
t x PH_3	0.189	0.198	0.220	0.224	0.194

* Corrected to O_2 = 10 mm.

The kinetics of the photosensitised reaction then are:-

$$-\frac{d[PH_3]}{dt} = R = \frac{[PH_3]}{[O_2]^2} \times \text{constant.}$$

This does not decide definitely which case is applicable to the reaction, since case 3 and case 6 lead to the same equation of initiation is due in the first to oxygen, and in the second to phosphine.

INERT GASES.

In Table XXII three series of results are listed for a constant oxygen pressure and for different argon pressures. First of all it is seen that argon inhibits the oxidation although in comparison with oxygen it does not quench mercury resonance radiation. The inhibition must therefore be due to chain termination, and since the value of $(\frac{1}{R} - \frac{1}{Ro})/p_A$ is constant, the inhibition term in the kinetic equation can be expressed in two ways, viz.,

$$K_{10}[Xo][A] \quad \text{or} \quad k_{11}[Xo][O_2][A]$$

Similarly there is inhibition by nitrogen, and again according to the same law. Until a decision is made about the mechanism of termination, no calculation can be made of the coefficients k_{10} and k_{11}.

In the kinetic equations, both cases 3 and 6 allow of the introduction of an inhibitory term containing both oxygen and inert gas. The inhibition by inert gases practically excludes cases 1 and 4, for it is probable, although the evidence is indirect, that the chain carriers are not excited molecules of very short life, and hence collision of Xp or Xo with argon or nitrogen should not lead to destruction of the carrier.

DIRECT PHOTOCHEMICAL OXIDATION.

The number of mechanisms has now been reduced to two. Fortunately the kinetic equations for the direct oxidation are different for cases 3 and 6, and thus it should be possible to decide which mechanism is applicable. Intensity measurements were not considered to be necessary in view of the definite results obtained with the photosensitised experiments. In Tables XXIV (Page 100) and XXV (Page 101) the complete data are given for varying oxygen and phosphine pressures.

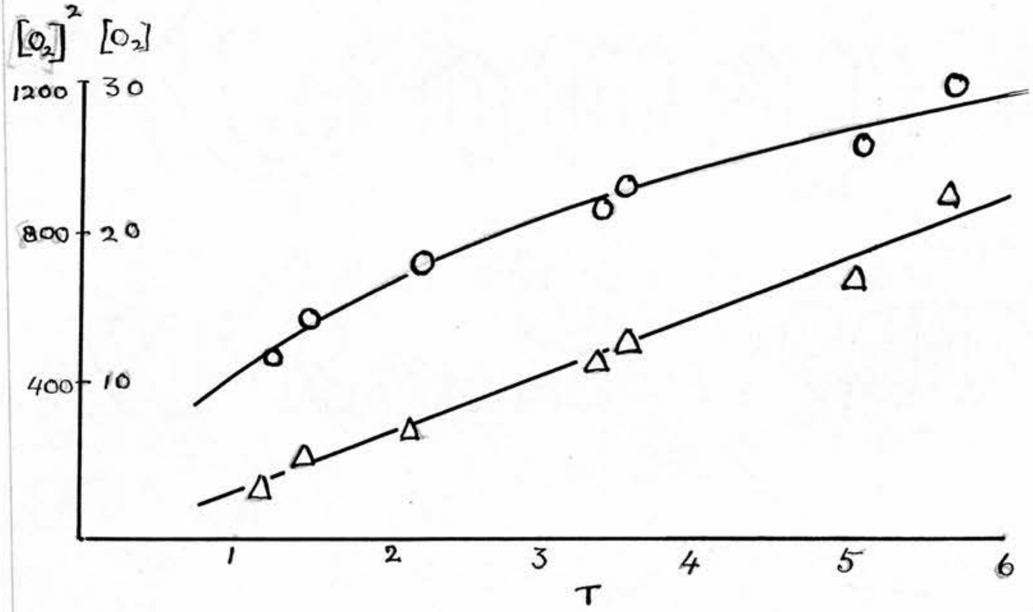


Fig 12

TABLE XXII.

Effect of Argon.

p PH_3	p O_2	p A	R	$\frac{1}{R}$	$(\frac{1}{R} - \frac{1}{R_o})/A$	t for $\Delta\rho$ = 0.039	$\frac{k_{10}}{k_6}$
0.260	25.0	55.0	0.0086	116.2	1.5	4.50	1.0
0.260	24.7	0	0.0285	35.1	-	1.45	-
0.263	25.7	14.6	0.0193	51.8	1.2	2.20	0.8
0.263	14.9	16.1	0.051	19.6	0.52	0.82	0.8
0.262	15.0	0	0.093	10.8	-	0.41	-
0.258	15.6	26.4	0.033	30.3	0.74	1.18	1.0
0.262	15.5	7.7	0.066	15.2	0.57	0.64	0.8
0.261	14.6	44.9	0.018	55.5	0.82	4.00	0.7
0.262	15.8	16.4	0.028	35.3	1.0	2.47	0.9
0.261	15.8	0	0.053	18.3	-	1.27	-

TABLE XXIV.

Direct reaction. Effect of oxygen.

PH_3	0.267	0.271	0.255	0.267	0.247	0.260	0.270
O_2	11.61	23.03	26.34	14.63	30.97	21.64	16.93
t.	$\Delta\rho$	$\Delta\rho$	$\Delta\rho$	$\Delta\rho$	$\Delta\rho$	$\Delta\rho$	$\Delta\rho$
0.25	0.037	0.012	0.009	0.025	-	-	0.021
0.5	0.062	0.022	0.016	0.043	-	0.016	0.035
1.0	0.092	0.035	0.029	0.076	0.025	0.035	0.060
1.5	0.116	0.052	0.042	0.102	0.035	0.052	0.079
2	0.134	0.067	0.051	0.120	0.042	0.069	0.092
3	0.165	0.089	0.067	0.156	0.062	0.092	0.119
4	-	0.107	-	-	0.079	-	0.144
5	0.205	0.127	0.102	0.201	0.092	0.127	0.158
R	0.131	0.0353	0.029	0.082	0.023	0.043	0.068
$\frac{1}{R}$	7.6	28.3	34.4	12.2	43.5	23.2	14.7
t	1.20	3.55	5.1	1.46	5.7	3.40	2.20

TABLE XXV.

Effect of phosphine.

p_{PH_3}	p_{O_2}	t for Δp = 0.025 mm. sec.	t x $p_{PH_3}^2$
0.130	17.3	108	1.82
0.535	17.7	7	2.00
0.275	17.4	26	1.97
0.131	17.2	85	1.46
0.391	17.3	10	1.53
0.261	17.3	20	1.36

In fig. 12 , $\frac{1}{R}$ and t for Δp = 0.100 mm. have been plotted against $[O_2]^2$ and also against $[O_2]$. The line obtained with the $[O_2]^2$ and also the constancy of the product t x $[PH_3]^2$ indicates that the kinetics in this pressure range can be summarised by the equation:-

$$- \frac{d[PH_3]}{dt} = R = \frac{[PH_3]^2}{[O_2]^2} \times \text{constant.}$$

Referring back to the theory given above it will be observed that the equation only agrees with case 3, and therefore the conclusion which may be drawn is that above the upper limit the chains are terminated by a triple collision between the chain carrier Xo and the two oxygen molecules. This is in agreement with the upper explosion limit data.[7]

It is now possible to return to the question of inhibition by argon and nitrogen. The plots of $\frac{1}{R}$ against A are straight, and hence the inhibition term will contain a factor of the first power of $[A]$. It is of importance to observe that a quadratic $[A]^2$ need not be introduced. The most probable mechanism for termination is that an Xo radical must collide with an inert gas molecule and an oxygen molecule. The function of the inert gas may simply be to stabilise the complex $Xo + O_2$ and thus prevent Xo further propagating the chain. Let the inhibition factor be $k_{10}[Xo][A][O_2]$, then k_{10} may be evaluated in the following way:-

Inserting this term in the equation for $[Xo]$ in addition to the term required by case 3.

$$-\frac{d[PH_3]}{dt} = R = \frac{k[PH_3]\,I\,[A]}{[O_2]\{k_6\{[O_2] + k_{10}[A]\}}$$

Hence $$\frac{1/R}{1/Ro} = 1 \quad \frac{k_{10}[A]}{k\ [O_2]}$$

where the subscript "o" refers to the runs done in absence of inert gas. From this equation the values of $\frac{k_{10}}{k_6}$ have been calculated and are given in Table XXII. Argon and nitrogen are about as efficient as oxygen in promoting the stability of the complex.

The next question is to determine the absolute value of k_6 and of c. For this purpose the ratio of the rates of oxidation to the rate of decomposition for the photosensitised and for the direct reaction were measured. These data are given in Table XXVI.

TABLE XXVI.

Chain length experiments.

Photosensitised reaction.

PH_3	O_2	Rate	Ratio of Rates	Chain Length	Chain Length at 5mm PH_3 & 50mm O_2
1.98	37.5	0.93×10^{-2} mm. per min. in 85 c.c. $I = 0.15$	19.2	38	53

PH_3	O_2	Rate	Ratio of rates.	Chain Length.	Chain length. at 5mm PH_3 & 50mm O_2
2.00	-	5.3×10^{-4} mm. in 514 c.c. I = 1.00			
8.0	81.0	3×10^{-2} in 85 c.c. I = 0.15	10.4	21	34
8.0	-	3.2×10^{-3} in 514 c.c. I = 1.00			
6.8	68	8.4×10^{-2}	8.4	17	43
6.7	-	11×10^{-3}			
Below lower limit.					
0.85	0.36	6.7×10^{-2} I = 0.15	480	960	820
0.79	-	0.93×10^{-2}			
0.83		0.93×10^{-2}	504	1000	830
0.83		2.52×10^{-2} I = 0.15 ✱			

✱ Ratio of lamp distances $\frac{66}{12.5}$

Direct reaction.

Below lower limit.

0.254	-	0.075	155	310	1200
0.254	0.237	11.6			
0.261	-	0.070	200	400	800
Above upper limit.					
8.23	121.4	54.0	36	72	210
8.64	-	1.5			
8.35	138.1	38.8	23.5	47	220
8.40		1.65			

Some notes of the experimental procedure adopted during these experiments may be mentioned here. Since the ratio of the rates of decomposition and oxidation was large, the rate of decomposition was measured by a McLeod gauge, and during the oxidation experiments a filter was employed to cut down the light intensity. In the direct reaction, comparison was made directly on the oil manometer. The rate of decomposition of phosphine was determined by measuring the pressure of hydrogen after the phosphine had been condensed out with liquid air. The ratio of rates is doubled to give the chain length, for the quantum yield of the dissociation is 0.5.

DISCUSSION.

First of all, it will be seen that below the lower limit, the chain lengths for the direct and photosensitised reactions are approximately the same. Above the upper limit, however, the chain length, calculated from the relative velocities in the direct oxidation is about five times that obtained in the sensitissed oxidation. This confirms the kinetic results about initiation by oxygen, and moreover gives the value of c, the number of chains started per excited mercury atom deactivated by oxygen; it is 0.2. There is some doubt as to the products of reaction when a 2^3P_1 mercury atom is deactivated by an oxygen molecule. If the low efficiency of initiation were due to deactivation, by collision or radiation, of an excited oxygen molecule of very short life, and if initiation be brought about by collision of this excited molecule with phosphine, then it is easily shown from the kinetic equations that the initiation factor takes the form $[PH_3]/[O_2]$, and hence:-

$$-\frac{d[PH_3]}{dt} = \text{constant} \times \frac{[PH_3]^2}{[O_2]^3}.$$

This does not agree with experiment. Some atom or molecule must emerge from the collision which is not subject to such easy removal as by an excited O_2 molecule; the most probable reaction is:-

$$Hg + O_2 \rightarrow HgO + O$$

The O atom reacting with the first phosphine molecule it encounters. In support of this it has been shown that illumination of oxygen-mercury vapour mixtures produces oxide of mercury.[59.]

One of the consequences of the theory of branched chains is that the explosion limit curve is a line of equal chain length. Therefore if the chain length be calculated below the lower limit and above the upper limit, and the values obtained extrapolated to the limits using the appropriate equations, the values obtained should be similar. The results of such a calculation are given in Table XXVI. Although the values of ν are of the same order of magnitude, it must be pointed out that at the upper limit, the chain length is 1/5 that at the lower limit.

As pointed out in the introduction, the value of

k_6 can be found from the equation:

$$k_6 = \frac{K'}{[O_2]_2^2 \times [O_2]_1},$$

and so the efficiency of the trimolecular collisions $Xo + O_2 + O_2$ can be found. Semenoff[56.] has made these calculations using Dalton's results, and finds that 0.4 ternary collisions are effective.

The value of k_6 can also be calculated in the two following ways, using the values of the chain length.

As pointed out before:

$$\nu = \frac{\text{oxidation}}{\text{decomposition}} = \frac{k_3 [PH_3]}{k_6 [O_2]^2}.$$

Now from Table XXVI, = 200 PH_3 = 8.4 and O_2 = 138.1

Then $\frac{k_3}{k_6 [O_2]}$ = 3300.

Since the propagation collisions are nearly 100% efficient, 3300 represents the ratio of the number of bimolecular to trimolecular collisions at 146.5 mm. pressure. Now it is assumed that at atmospheric pressure, this ratio is 10^3, so at 146 mm. it will be 760/146.5 x 10^3 = 5200, and therefore the ratio $\frac{3300}{5200}$ = 0.6 gives the probability that the ternary collision $Xo + O_2 + O_2$ results in destruction of Xo.

This result may also be checked by the equation of the explosion limit (equation 12),

$$(\alpha - 1) k_3 \, PH_3 = k_6 [O_2]^2.$$

To calculate $\frac{k_3}{k_6 \, O_2}$ from this expression, the value of $(\alpha - 1)$, the probability of branching, must be known. The chain length is 10^3 at the lower limit and 2 x 10^2 at the upper limit, and the probabilities of branching, 10^{-3} and 5 x 10^{-3} respectively. At the upper limit (5mm. PH_3 and 50 mm. O_2):-

$$\frac{k_3}{k_6\ O_2} \text{ is } \frac{50}{10^{-3} \times 5} \text{ or } \frac{50}{10^{-3} \times 5 \times 5} = 10^4 \text{ or } 2 \times 10^3$$

At 55 mm. pressure, the ratio of bi- to tri-molecular collisions is 1.5 x 10^4, which gives the value of the efficiency of the collisions Xo O_2 O_2 as 0.67 (if the chain length below the lower limit be used) or 0.13 if 200 be taken as the chain length. This latter value is in agreement with that given by Semenoff in a monograph as yet unpublished.

There is yet another check on the inter-relationship between the stable and explosive reactions. The whole explosion curve may be represented by the equation obtained on adding (9) and (12).

$$2(\alpha - 1)\ k_3[PH_3] = \frac{K'}{[O_2]} + k_6[O_2]^2 \quad . \quad . \quad . \quad . \quad 21$$

For $[PH_3]$ to be a minimum then by differentiating this equation with respect to $[O_2]$ and equating to zero:-

$$[O_2] = \sqrt[3]{\frac{K'}{2k_6}}$$

From the results shown in fig. 13, the minimum occurs at 462 mm. O_2.

Similarly for the reaction outside the limits, the values of ν below and above the limits respectively are given by:-

$$\nu_{\text{below}} = \frac{k_3}{K'}[PH_3][O_2]$$

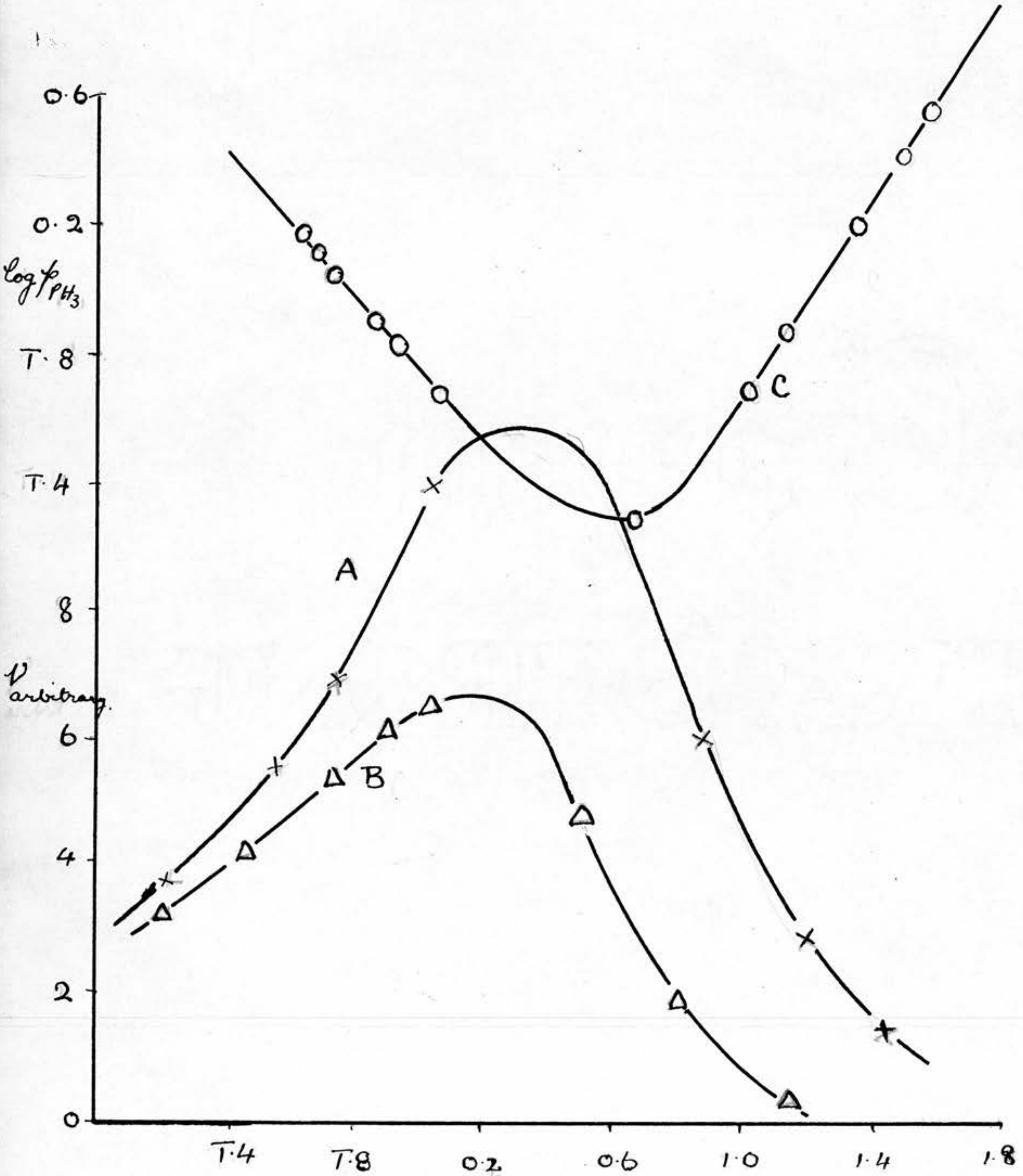


Fig 13.

A. Photosensitised Reaction
B Direct Photo "
C Exp. Limit curve.

$$\nu_{\text{above}} = \frac{k_3[PH_3]}{k_6[O_2]^2}$$

$$\text{or} \quad \nu = k_3[PH_3]\left\{\frac{[O_2]}{K'} + \frac{1}{k_6[O_2]^2}\right\}$$

$$\frac{d\nu}{dO_2} = \frac{k_3}{K'}[PH_3] - \frac{2k_3[PH_3]}{k_6[O_2]^3}$$

This expression equals zero when ν is at a maximum.

$$\text{Then} \quad [O_2] = \sqrt[3]{\frac{K'}{2k_6}} \; .$$

Thus the maximum in the chain length curve should occur at the same oxygen pressure as the minimum in the explosion curve. Fig. 13 shows that these anticipations are fairly exactly justified experimentally. 57. In the figure of the preliminary notice of this work the rate of reaction was plotted against the pressure of the oxygen but it was also pointed out that the curve would have to be suitably corrected for deactivation of the mercury atoms by oxygen. On account of initiation by oxygen, however, the corrections to be made are small, so that the curve does represent the variation of chain length with pressure.

This is easily seen from Table XXVII, where the v value of the initiation expression:

$$\frac{F(c)}{I} \qquad \frac{[PH_3] + c.0.5[O_2]}{[PH_3] + 0.5\,O_2 + 0.37}$$

is given for various oxygen pressures.

The results of the photosensitised results are also plotted in fig. 13. The position of the minimum in the explosion curve, which is 0.212 mm. PH_3 and 4.62 O_2, was calculated from equations. 21

TABLE XXVII.

PH_3 = 0.1 mm.

O_2	0.05	0.1	0.2	0.5	1.0	2.0	5.0	10.0	50.0
$\frac{(c)}{l}$	0.20	0.21	0.21	0.21	0.21	0.20	0.20	0.20	0.20

Effect of rate of starting on the position of the explosion limits.

Excepting for the moment the oxidation of phosphorus and of phosphine, there is abundant evidence that the position of both limits is dependent on the rate at which chains are started. In the hydrogen oxygen reaction, for example, it has been shown that hydrogen a atoms, produced photochemically,[60.] thermally,[18.] and electrically,[19.] oxygen atoms,[19.56.] and chlorine atoms[63.] all reduce the temperature of spontaneous ignition. Moreover, even at room temperature, conditions simulating a lower limit may be obtained with a spark used to start the cha chains.[62.] The action of nitrogen peroxide in reducing the ignition temperature of H_2, CO, CH_4 etc., is also a question of rate of starting affecting the limits. Similarly the limits in the oxidation of sulphur, carbon disulphide and hydrogen sulphide may be considerably reduced by suitable stimuli. More examples may easily be quoted, but the situation may be summed up by the statement that in those reactions where the limits are temperature dependent, and where the explosion occurs at high temperatures (say about 200°C), the position of both lower and upper limits is dependent to some extent on the rate of initiation. The pure chain hypothesis does not therefore wholly express the condition for explosion: in addition some temperature dependent factor must be introduced to provide an explanation. With phosphorus and phosphine it is different, the propagating collisions are almost 100% efficient, and the efficiency of branching is so high that it cannot be dependent on temperature to any great degree. Similarly the termination reactions at the walls are independent of temperature. In these two examples, them, it is to be expected that the pure chain explosion would occur, and that the condition is expressed adequately by the statement that the product of the probability of branching and the probability of termination is equal to unity, from which it at once follows that the explosion pressures should be independent of the rate of starting. The test is consequently rather a crucial one for some sections of the chain theory. Some time ago it was applied to the lower limit of phosphine[63], and a considerable lowering of the limit was obtained. The curious fact was that the effect persisted for a time greater than the life of the reaction chains. Later it was shown by Melville[32] to be wholly due to an alteration in the surface upon which the chains terminated. In the experimants described below, the experiments have been repeated at the upper limit, where, of course, wall action has no effect. Initiation was effected by means of the light from the water cooled mercury lamp.

Some hint of the behaviour to be expected has been got when it is seen that the chain lengths at the upper and lower limits are not identical. Apparently the explosion can occur more readily at high pressure, in that such a high chain length is not necessary.

Preliminary experiments at once showed that there was a considerable displacement of the upper limit to higher pressures when the tube is illuminated. Some experiments were done to find if this effect was at all lasting, by shutting off the light just before explosion was due. The limit in these experiments was found to be the same as when the gases were not illuminated. Table XXVIII gives a number of typical results.

TABLE XXVIII.

	Initial Pressures.		Total p. at Expl.			Condition of Illumination
	PH_3	O_2		PH_3	O_2	
1.	6.5	103	72	4.5	67.5	During expansion.
2.	6.4	99	26	1.7	24.3	None
3.	6.6	99.5	26	1.7	24.3	See text
4.	5.3	103	57.3	2.9	54.4	During ex-
		112	65			pansion
5.	6.4	112	65	3.7	61.3	"
6.	4.7	95	56.5	2.8	53.7	"

Effect of variation of light intensity.

					Intensity.
7.5	113	63.5	4.2	59.3	1.00
7.5	113	43.5	2.9	40.6	0.15
6.5	100	38.5	2.5	36.0	0.15
7.4	100	56.5	4.2	52.3	0.15
7.3	106	63.5	4.4	59.1	1.00
4.8	111	42.3	1.8	40.5	1.00
8.1	101	80.0	6.0	74.0	1.00

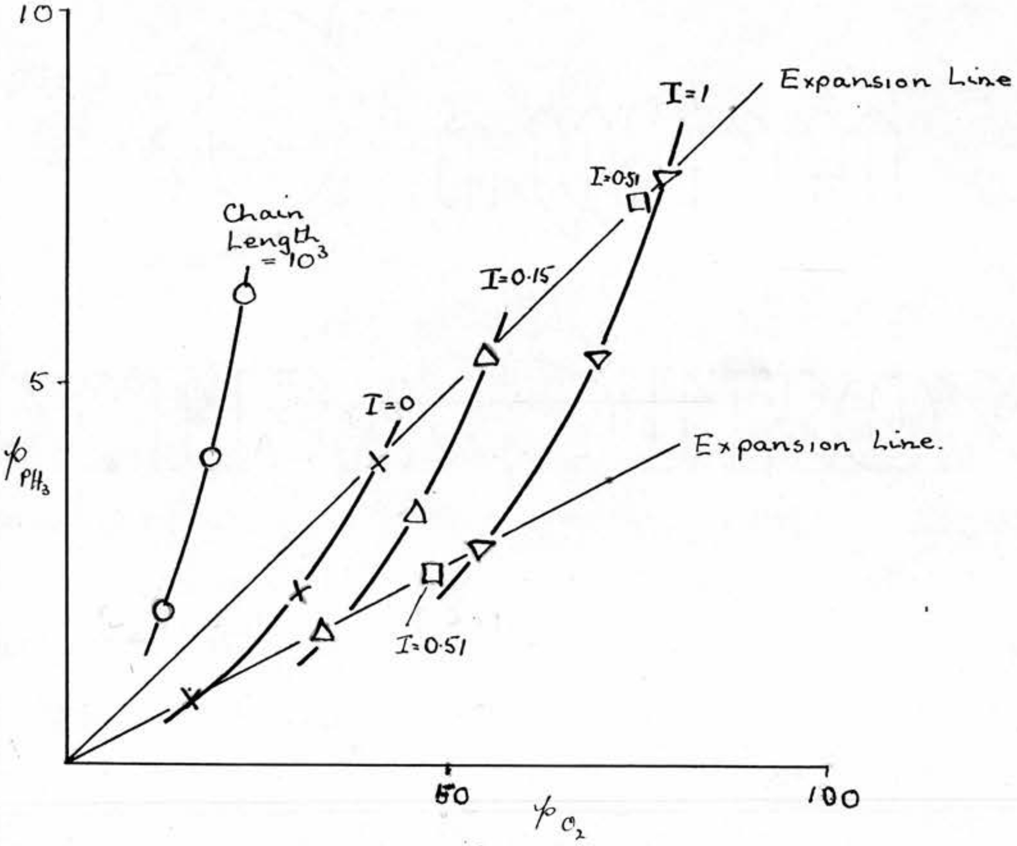

10
5
p_{PH_3}
50
100
p_{O_2}
Chain Length $= 10^3$
I=0
I=0.15
I=0.51
I=1
I=0.51
Expansion Line
Expansion Line.

Fig. 14

Rate of stable reaction at initial pressure
= 0.013 mm. per min.

I = 1.00

Experiments 1-3 may be particularly mentioned. The initial pressures were all practically the same, but the explosion pressure has been increased from 26 mm. in no. 2 to 72 mm. in no.1. In experiment 3 illumination was carried on until the pressure was reduced to 74 mm. The explosion did not take place until a pressure of 26 mm. was reached. The time required for the pressure to fall from 74 mm. to 72 mm. was not more than two secs. It is therefore quite different from the lower limit phenomenon which persists for several minutes. It will be also noted that variation of intensity has an effect on the limit.

The effect of intensity was further investigated in the following way. Instead of plotting upper limit curves for different intensities, two sets of mixtures of constant composition were used. Since expansion does not alter the composition of the mixture, the displacement of the explosion limit along the expansion line can be regarded as a measure of the effect. The data are given in Table XXIX and plotted in fig. 14.

The intensity could not be increased to higher values as then the velocity of the reaction was sufficient to remove appreciable amounts of phosphine.

These results then prompt a further question as to whether, at the lower limit, in addition to the ordinary displacement owing to the change in surface, there is a transient effect similar to that at high pressure. The procedure adopted was to use a constant pressure of phosphine and allow oxygen to leak in through the needle valve and record the explosion pressure on the oil manometer. The intensity of illumination was 0.15 on the same scale as Table XXIX.

TABLE XXIX.

Original Pressure.		Pressure at Explosion.			Intensity.
PH_3	Total	Total	PH_3	O_2	
8.9	97.6	28	2.6	25.4	0
12.5	155.	73	5.9	67	1.0
12.6	141	60	5.4	55	0.15
12.6	139	44	4.0	40	0
13.0	147	85	7.5	77.5	1.00
12.9	142	83	7.5	75.5	0.51
5.2	117	12	0.53	11.5	0
5.3	103	55	2.8	52	1.00
5.1	99.	51	2.6	48.4	0.51
5.1	95	42.5	2.2	40.3	0.15
5.0	98	52	2.7	49.3	1.68
5.0	90	52	2.9	49.1	11.2
5.0	92	47	2.6	44.4	11.2
5.0	92	15	0.82	14.2	0
11.2	138	92	7.5	84.5	11.2
12.9	146	79	7.0	72.0	11.2

TABLE XXX.

	PH_3	O_2 at exp.	P Total	Conditions of illumination
1	0.74	0.61	1.35	Continuous
2	0.81	0.54	1.35	Until P = 1.26
3	0.80	0.49	1.29	" P = 1.26
4	0.80	0.79	1.59	None
5	0.77	0.76	1.53	None
6	0.80	0.49	1.29	Until P = 1.26
7	0.78	0.48	1.26	Continuous
8	0.76	0.44	1.20	Until P = 1.18
9	0.76	0.64	1.40	" P = 1.12
10	0.76	0.48	1.24	" P = 1.18
11	0.76	0.64	1.40	" P = 1.12
12	0.77	0.74	1.51	None

Comparing Nos. 4,5 and 12 with the remainder, it is seen that explosion pressures are somewhat higher in these cases than when the mixture has been illuminated. However it does not appear to matter whether the light is switched off some time before explosion or whether it is left on right up to the limit. It will also be noticed that if illumination be stopped at low pressures of oxygen (exp. 9 and 11) the explosion limit is a little higher than that where illumination has been continued up to higher pressures.

The conclusion, then, is that the transient effect obtianed at the upper limit is not in evidence at the lower limit.

To demonstrate more clearly the sensitiveness of the upper limit to the stationary concentration of Xo, the following experiment and calculations were made. A mixture of 12.0 mm. phosphine and 134 mm. argon was made up and illuminated during expansion. Explosion occurred at 60 mm. The intensity of the light was 0.15, on the same scale as Table XXIX. A second similar mixture was then prepared and pumped down to 63 mm; at this pressure the rate of oxidation of phosphine was 10.7 x 10^{-5} mm. per sec. in a volume of 85cc; the calculated chain length is 10^2. The number of quanta entering the tube per sec. is thus about $10^{23} \times 10^{-4} \times 10^{-2} = 10^{17}$.

Now at 65 mm. pressure a molecule experiences about 10^6 ternary collisions per second. Thus the mean life of an Xo molecule, assuming it to be destroyed in every ternary collision of the type Xo + X + X, is 10^{-6}. The rate of production of Xo may be taken as the rate of dissociation of the phosphine $= \frac{10.7 \times 10^{-5}}{10^{2}} = 10^{-6}$ mm. per sec. and the stationary concentration of Xo is thus 10^{-12} mm.

According to Table XXIX, then, when the concentration reaches about 10^{-11}mm., the Limit ceases to be effected. When such a small concentration of carrier displaces the limit so much, it is not surprising that traces of water vapour and changes of temperature[7.] exert a comparatively large influence. This in turn suggests that the displaced limit is the true limit, and that the one observed in the thermal reaction is particularly low because of the fact that a sufficient number of chains do not start to fulfil the conditions of the chain theory. If this were the case the chain length at the limit should be 10^{3}, whereas it is only about 10^{2}. The displacement cannot be due to the pressure of ozone which is formed when the chains are terminated, for if this were so, the effect would persist after the light is switched off.

In order to get a further insight into this problem, the following experiments were done. Mixtures of oxygen and phosphine, one above the upper limit, and the other below the lower limit, were made up in silica tubes and placed beside a quantum counter in order to find if the stable reaction was appreciable without outside stimulus. Light given off by a phosphine explosion is greenish in colour, but there is associated with it some ultraviolet of sufficiently short wavelength to activate a counter. Neither of the two tubes had any effect on the counter, showing that the amount of light striking the counter was less than 10^2 quanta per minute.

SUMMARY.

The decomposition and oxidation of phosphine have been studied on the surface of tungsten and molybdenum filaments, with a view to using a filament method to investigate the kinetics of the chain reaction between phosphine and oxygen. This method was found to be unsuitable as the oxidation took place almost entirely on the surface of the filament. The surface oxidation and decomposition were however studied and a theory put forward to account for the difference in behaviour of phosphine and phosphorus. A simple means of correcting for end losses in a hot filament is described.

In Part Two the kinetics of the phosphine oxidation outside the explosion limits have been studied using the mercury sensitised reaction and the direct photochemical reaction as means of investigation. The particular investigation carried out is that of the means of termination of chains at and above the upper explosion limit. The results work out in agreement with Dalton's work on the explosion limit; the chain carriers Xo

is destroyed in a three body collision of the type $Xo + O_2 + X$, where X is any molecule capable of stabilising the $Xo - O_2$ complex. The efficiency of this collision is of the order 0.4.

Experiments have also been done on the effect of illumination on the upper limit. It is quite clear that the intensity of illumination has an effect on the upper limit and tends to aid explosion. The tentative suggestion is put forward that the limit obtained without illumination is not the true chain theory explosion limit, as the rate of starting of chains is not then sufficient for the relationship to hold good. Quantum counter experiments are in support of this.

The author is deeply indebted to Dr H. W. Melville and Dr E. B. Ludlam for continuous advice and encouragement during this work and to the Trustees of the Moray Fund for a grant towards the cost of apparatus.

Thanks are also due to Dr Ouillet of Cambridge for carrying out the quantum counter experiments mentioned above.

REFERENCES.

1.Einstein. Ann. Physik. 37. 832, 38, 881, 1912.
2.Warburg. Summarised in Zeit. Elektrochen. 26, 54, 1920.
3.Nernst. Zeit Elektrochen. 1918, 24, 335.
4.Lindemann. Trans. Far. Soc. 1922, 17, 598.
Hinshelwood. Hutchison. Proc. Roy. Soc. 1926A, 111, 245, and others.
5.Christiansen and Kramers. Zeit. Phys. Chem. 1923, 104, 451.
6.Melville. Trans. Far. Soc. 1932, 138, 128, 814.
7.Dalton. Proc. Roy. Soc. 1930A, 128, 263.
8.Semenoff. Zeit Physik. 1927, 46, 109, 1928, 48, 511.
9.Garner and Gomm. Trans. Far. Soc. 1928, 470
10.Bodenstein. Zeit. Phys. Chem. 1905, 53, 166.
11.Lewis and Feitknecht. J.A.C.S. 1931, 53, 2, 2910.
12.Schumacher and Steiger. Zeit. Phys. Chem. B7, 363.
13.Alyea and Haber. Zeit. Phys. Chem. 1930, 10B, 193.
14.Alyea. J.A.C.S. 1931, 53, 1, 1324.
15.Taylor and Lavin. J.A.C.S. 1930, 52, 1910.
16.Farkas, Haber and Harteck. Zeit Elektrochen, 1930, 36, 711.
17.Taylor and Salley. J.A.C.S. 55, 96, 1933.
18.Haber and Oppenheimer. Zeit. Phys. Chem. 1932, 16B, 773.
19.Semenoff, Nalbandjan and Dubowizky. Trans. Far. Soc. 1933, 29, 606.
20.Mitchell and Marshall. J.C.S. 1923, 123, 2448.
21.Taylor. J.A.C.S. 1926. 48, 2840.
22.Taylor. Chem Re . 1931. 9, 12.
23.Mecke. Zeit. Elektrochen. 1930, 36, 595.
24.Thompson. Zeit. Phys.Chem. 1930. 10B, 273.
25.Hinshelwood. Trans. Far. Soc. 1932, 28, 184.
26.Melville and Ludlam. Proc. Roy. Soc. 1932A, 135, 315.
27.Semenoff. Zeit. Phys. Chem. 1929, 2B, 161.

28. Ritchie. Proc. Roy. Soc. 1932, AB8, 635.

29. Ritchie, Brown and Muir. Proc. Roy. Soc. 1932, A137, 511.

30. Melville. Proc. Roy. Soc. 1932, A135, 315.

31. Melville. Proc. Roy. Soc. 1932, A138, 374.

32. Melville. Proc. Roy. Soc. 1933, A139, 541.

33. Cambridge Instrument Company Catalogue.

34. Melville. Proc. Roy. Soc. 1932A, 138, 394.

35. Preuner and Brockmoller. Zeit. Phys. Chem. 1931, 81, 159.

36. Jakolewa. Zeit. Physik. 1931, 69, 548.

39. Melville. Trans. Far. Soc. 1932, 28, 131, 1.

40. Kunsman. J.A.C.S. 1928, 50, 2100.

41. Kunsman. Phil. Mag. 1930, 10, 1015.

43. Melville. Trans. Far. Soc. 1932, 28, 885.

44. Frankenburger and Hodler. Trans. Far. Soc. 1932, 28, 229.

45. Hailes. Trans. Far. Soc. 1931, 124, 601.

46. Taylor. J.A.C.S. 1930, 53, 578.

47. Hinshelwood and Burk. J.C.S. 1925, 127, 1105.

48. Dalton and Hinshelwood. Proc. Roy. Soc. 1929, A125, 294.

49. Hollaender and Foerst. Rev. Sc. Inst. 1933, 4, 347.

50. Melville and Walls. Trans. Far. Soc. 1933, 150, 29, 1255.

51. Gibson and Hinshelwood. Trans. Far. Soc. 1928, 24, 559.

52. Hinshelwood. Kinetics, Third Edition.

53. Garstang and Hinshelwood. Proc. Roy. Soc. 1931A, 134.

54. Hadow and Hinshelwood. Proc. Roy. Soc. 1931A, 132, 375.

55. Semenoff. Zeit. für Physik, 1930, B6, 307.

56. Semenoff. Phys. Zeit.Sov. 4, 709, 1933, 4, 723, 1933.

57. Melville and Roxburgh. Nature. 1933, 131, 690.

58. Grant and Hinshelwood. Proc. Roy. Soc. 1933, 141, 29.

59. Dickenson and Sherrill. Proc. Nat. Acad. Sc. 1926. 12, 175.

60. Bates and Salley. J.A.C.S. 1933, 55, 110.

61. Norrish. Proc. Roy. Soc. 1931, A135, 334.

62. Thompson. Trans. Far. Soc. 1933, 28, 299.

63. Clusius and Hinshelwood, Proc. Roy. Soc. 1930 A 129, 589.