66. *The Oxidation of Phosphine in Presence of Tungsten and Molybdenum.*

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In a previous paper (J., 1933, 586) we described the investigation of the kinetics of the thermal decomposition of phosphine on tungsten and molybdenum 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 with phosphorus–oxygen mixtures (Melville and Ludlam, *Proc. Roy. Soc.*, 1932, *A*, **135**, 315). Further, it was suggested, to account for the formation of red phosphorus in the decomposition, that P_2 molecules may evaporate off the filament. As it has been shown that such molecules initiate chains in phosphorus–oxygen mixtures, 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-initiating molecules. Other possibilities are discussed below (p. 270).

Three criteria exist whereby the chain character of the reaction may be determined, (*a*) the appearance of a glow, the intensity of which is proportional to the rate of oxidation, (*b*) the acceleration of the reaction by use of wider tubes, and (*c*) the acceleration produced by the addition of inert gases. These 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, nor would the acceleration by inert gases be so marked. Owing to the variation in the condition of the surface of the reaction tube, it is sometimes difficult to verify the diameter law, and therefore in the present instance, the inert-gas effect has been used to determine what fraction, if any, consisted 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, for it has been shown in the phosphorus experiments (*loc. cit.*, p. 327) that the observed increase in velocity is in agreement with the value calculated from the diffusion theory.

Experimental.

The apparatus was identical with that described in the first paper, and the same type of divided filament was used to measure its temperature. The pressures which could be employed were, of course, now restricted by the occurrence of explosion at 1 mm. for the 1 : 1 mixture. An oil manometer was used for the majority of the experiments. Both molybdenum and tungsten were apparently unattacked by the products of the reaction for, on examination of the filament surface by a microscope, no pitting or roughening could be observed, and the diameter remained the same throughout a long series of experiments. It was observed, however, that the activity of the wire gradually diminished with use, but could easily be restored by heating in a vacuum at about 1000° for a few minutes. Between each run, the filament was glowed at this temperature, and it will be shown below that this procedure renders the 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 $PH_3 + O_2 \longrightarrow HPO_2 + H_2$, whereas with a large excess a more highly oxidised phosphorus acid is obtained and the amount of hydrogen produced is not proportional to that of oxygen used. With equivalent proportions, the rate might be measured by finding the decrease in phosphine or oxygen pressure, or alternatively, the increase in hydrogen pressure. In addition, as HPO_2 has an inappreciable vapour pressure as measured by the oil manometer, there will be a decrease in pressure during the reaction which may also be used as a measure of its extent. To find which of these methods would prove most suitable, analyses were made of the phosphine–hydrogen–oxygen mixtures at various stages in the reaction and with different proportions of phosphine and of 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 made in order to determine whether the residual gas after the first combustion was hydrogen or oxygen.

TABLE I.

Temp. of filament, 836° K.; * length, 15 cm.; diam., 0·01 cm.; vol. of apparatus, 230 c.c.; press. in mm. Hg.

Expt. No.	*t*.	p_{PH_3}.	p_{O_2}.	Final press.	Δp.	$p_{N.C.}$.†	Δp_{PH_3}.	p_{H_2}.	p_{O_2}.
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
180	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	—	—
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.

† $p_{N.C.}$ = Press. of non-condensable gas.

Table I gives the complete results for a number of runs with a molybdenum filament, time (*t*) being expressed in minutes. The procedure was as follows: Phosphine was passed into the reaction tube and its pressure measured; this was followed by oxygen; the filament was heated for the required time, and the pressure again determined. Liquid air was applied to a small side tube to condense the phosphine in order to find the pressure of hydrogen and oxygen. As the vapour pressure of phosphine at liquid-air temperatures is only 0·007 mm., the pressures read on the manometer were reduced by this amount. 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. Δp is the change in total pressure and Δp_{PH_3} the decrease in phosphine pressure calculated from the manometer readings. Unfortunately, the analysis of the hydrogen–oxygen mixtures was not very accurate, for after compression into the combustion bulb, the pressure was only about 10 mm. or less; the results are probably only accurate to 10%.

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

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

For comparison, a similar set of experiments with a tungsten filament is given in Table II. The results are essentially similar; even with a 1 : 1 mixture, there is no very close correspondence between Δp, Δp_{PH_3}, and p_{H_2}, which would be the case if hydrogen and HPO_2 were the only products. In subsequent experiments to determine the kinetics of the reaction, analysis of the mixture was effected by condensing out the phosphine, after which the side tube was warmed, and a short time (5 mins.) allowed for the gases to mix completely before the current was started in the filament again.

TABLE II.

Temp. of filament 768° K. Dimensions as in Table I.

Expt. No.	t.	p_{PH_3}.	p_{O_2}.	Final press.	Δp.	$p_{N.C.}$.	Δp_{PH_3}.	p_{H_2}.	p_{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

In Table I, the pressure of phosphine remained constant and that of oxygen was varied; in Table III, some additional runs are recorded as well as a decomposition run in order to find by how much the rate of oxidation was faster than the decomposition. Table IV gives a number of experiments in which the pressure of oxygen remained constant and that of phosphine was varied.

TABLE III.

Same experimental conditions, molybdenum filament.

	p_{PH_3}, 0·425; p_{O_2}, 0·406.			p_{PH_3}, 0·403; p_{O_2}, 0·095.			p_{PH_3}, 0·403.
t.	p.	p_{PH_3}.	Δp_{PH_3}.	p.	p_{PH_3}.	Δp_{PH_3}.	Δp_{PH_3}.
0	0·831	0·425	—	0·498	0·403	—	—
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

TABLE IV.

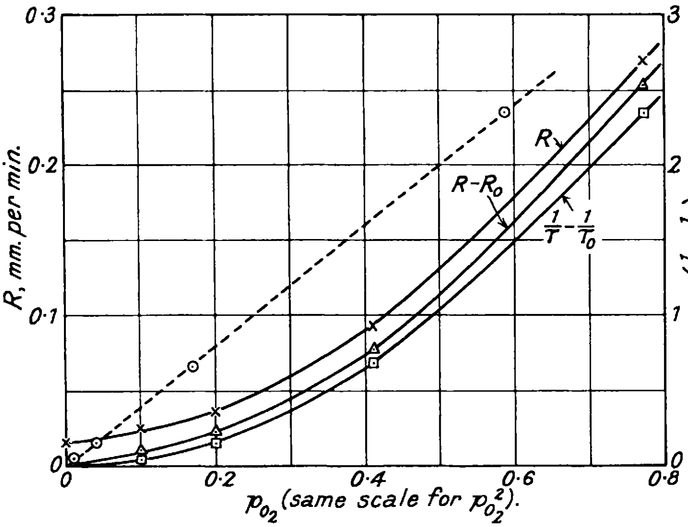
p_{PH_3} p_{O_2}	0·114 0·376			0·200 0·376			0·782 0·372			0·397 0·371		
t.	p.	p_{PH_3}.	Δp_{PH_3}.	p.	p_{PH_3}.	Δp_{PH_3}.	p.	p_{PH_3}.	Δp_{PH_3}.	p.	p_{PH_3}.	Δp_{PH_3}.
0	0·490	0·114	—	0·576	0·200	—	1·154	0·782	—	0·768	0·397	—
1	0·432	0·084	0·030	0·451	0·105	0·095	1·099	0·704	0·078	0·653	0·298	0·099
2	0·397	0·058	0·066	0·384	0·057	0·143	1·050	0·653	0·129	0·596	0·244	0·153
4	0·350	0·034	0·080	0·331	0·017	0·183	1·005	0·572	0·210	0·543	0·189	0·208
8	0·326	0·021	0·093	—	—	—	0·961	0·468	0·314	0·495	0·132	0·265

These data are plotted in Figs. 1 and 2. In the former, the initial rate (*R*), the initial rate minus the rate of decomposition of phosphine ($R - R_0$), and the quantity $1/\tau - 1/\tau_0$ (τ is the time required for Δp_{PH_3} to reach 1·0 mm. and τ_0 that for the decomposition) are plotted against p_{O_2}. The three methods of plotting the results give closely parallel curves and it may be concluded that the order with respect to the oxygen pressure is two, since on plotting $1/\tau - 1/\tau_0$ against $p^2_{O_2}$, the line obtained is straight. Inspection of Fig. 2, where Δp_{PH_3} is plotted against time for three different pressures of phosphine, shows that the order is nearly zero. Unfortunately, the kinetics cannot be extended to higher pressures owing to explosion.

During these experiments, it was observed that a faint glow accompanied their progress. There was thus an indication that part of the reaction was homogeneous. In Table V, therefore, three runs are given using the same pressures of phosphine and of oxygen; in Expt. 201, argon was present from the start, in Expt. 202 it was added after 3 mins.; Expt. 203 is a run without argon. In all cases, as the decrease in the pressure of phosphine 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 photochemical oxidation (Melville, *Proc. Roy. Soc.*, 1932, *A*, **138**, 389) below the lower limit.

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 can only form a very small part of the total. This is consistent with the fact that the intensity of the glow is even less than that in the oxidation of phosphorus, where the rate of oxidation was about 0·1 of that obtaining in the present experiments.

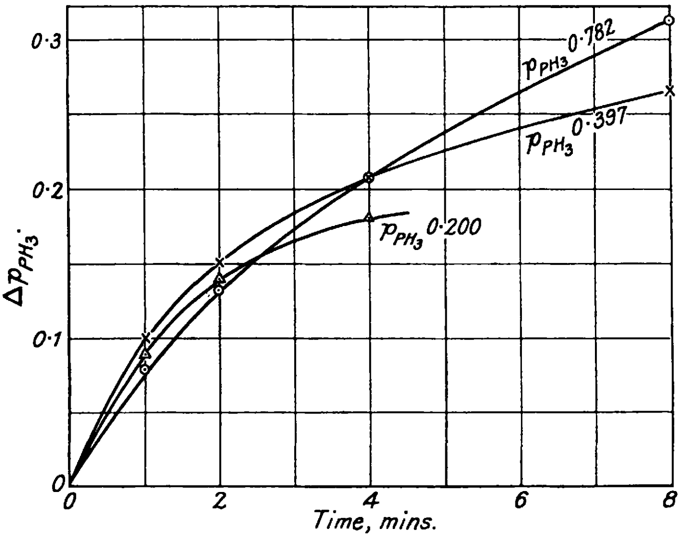
FIG. 1.



Broken line: graph of $1/\tau - 1/\tau_0$ *against* $p^2_{O_2}$.

Temperature coefficient. In order to ensure an accurate comparison, the apparent energies of activation (E) of the oxidation and decomposition were measured with the same specimen of wire, the one immediately after the other. The results are in Table VI, T being the absolute temperature.

FIG. 2.



Tungsten Filament.—The above experiments show that oxygen does not displace adsorbed phosphine from a molybdenum surface, since the rate of reaction is almost independent of p_{PH_3}, thus agreeing with the data 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

TABLE V.

Molybdenum filament; temp. 836° K.

	Expt. 201.			Expt. 202.			Expt. 203.		
p_{PH_3}		0·409			0·424			0·424	
p_{O_2}		0·380			0·375			0·375	
p_A		0·512			0·603			—	
$t.$	$p_{tot.}$.	p_{PH_3}.	Δp_{PH_3}.	$p_{tot.}$.*	p_{PH_3}.	Δp_{PH_3}.	$p_{tot.}$.	p_{PH_3}.	Δp_{PH_3}.
0	1·301	0·409	—	0·799	0·424	—	0·799	0·424	—
1	1·204	0·303	0·106	0·689	0·327	0·097	0·693	0·330	0·094
2	1·127	0·252	0·157	0·635	0·277	0·147	0·632	0·274	0·150
3	—	—	—	0·606	0·248	0·176	0·596	0·241	0·183
4	1·082	0·208	0·201	0·588	0·210	0·214	0·579	0·220	0·204
5	—	—	—	0·566	0·203	0·231	0·563	0·199	0·225
7	—	—	—	0·547	0·169	0·255	0·547	0·178	0·246
8	1·033	0·158	0·251	—	—	—	—	—	—

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

TABLE VI.

Expt. No.	p_{PH_3}.	p_{O_2}.	T.	$\log_{10}T_{1/4}$.	$\log_{10}T_{1/2}$.	E (kg.-cal.).
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	0·420	—	836	—	0·505	
290	0·420	—	793	—	0·820	
291	0·420	—	758	—	1·159	

$T_{1/4}$ is the time for 25% reaction, *i.e.*, for the consumption of 25% of the PH_3; $T_{1/2}$ is that for 50% reaction.

total order of the oxidation reaction would be 2 if the oxygen is not strongly adsorbed. The variation in rate with p_{PH_3} and p_{O_2} is given by the data in Table VII; the method of gas analysis was exactly the same as that adopted with molybdenum, including the glowing of the filament between the runs in order to obtain reproducible results.

TABLE VII.

Tungsten filament; temp. 768° K.

	Expt. 221. p_{PH_3}, 0·404; p_{O_2}, 0·411.				Expt. 222. p_{PH_3}, 0·403; p_{O_2}, 0·245.				Expt. 223. p_{PH_3}, 0·403; p_{O_2}, 0·084.			
$t.$	p.	Δp.	p_{PH_3}.	Δp_{PH_3}.	p.	Δp.	p_{PH_3}.	Δp_{PH_3}.	p.	Δp.	p_{PH_3}.	Δp_{PH_3}.
0	0·815	—	0·404	—	0·648	—	0·403	—	0·487	—	0·403	—
1	0·780	0·035	0·381	0·023	0·626	0·022	0·388	0·015	—	—	—	—
2	0·739	0·076	0·352	0·052	0·603	0·045	0·367	0·036	0·477	0·010	0·883	0·020
4	0·689	0·126	0·323	0·081	0·569	0·079	0·337	0·066	0·470	0·017	0·363	0·040
8	0·617	0·198	0·272	0·132	0·526	0·122	0·297	0·106	0·461	0·026	0·333	0·070

	Expt. 224. p_{PH_3}, 0·413; p_{O_2}, 0·819.				Expt. 227. p_{PH_3}, 0·127; p_{O_2}, 0·412.				Expt. 228. p_{PH_3}, 0·262; p_{O_2}, 0·411.			
0	1·232	—	0·413	—	0·539	—	0·127	—	0·673	—	0·262	—
1	1·163	0·069	0·371	0·042	—	—	—	—	0·636	0·037	0·254	0·008
2	—	—	—	—	0·483	0·056	0·101	0·026	0·607	0·066	0·223	0·039
4	1·020	0·212	0·269	0·144	0·449	0·090	0·081	0·046	0·564	0·107	0·190	0·072
8	0·892	0·340	0·184	0·229	0·398	0·141	0·051	0·076	0·506	0·167	0·147	0·115

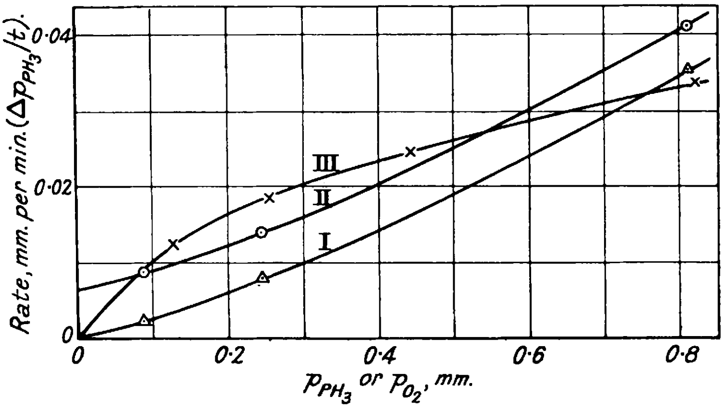
	Expt. 230. p_{PH_3}, 0·812; p_{O_2}, 0·398.				Expt. 225. p_{PH_3}, 0·420; p_{O_2}, —.	
0	1·210	—	0·812	—	0·420	—
1	1·190	0·020	0·786	0·026	—	—
2	1·159	0·051	0·737	0·075	0·407	0·013
4	1·123	0·087	0·712	0·100	0·398	0·022
8	1·061	0·149	0·649	0·163	0·368	0·052

The data of Table VII are plotted in Fig. 3. Curve I is the R–p_{O_2} graph, and II the $(R - R_0)$–p_{O_2} graph. The rate is nearly proportional to p_{O_2}, contrasted with the bimolecular course found for molybdenum. Curve III is for various 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 is 0·5, and therefore $R \approx p_{PH_3}^{1/2}$.

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. The pressures employed were 0·4 mm. of phosphine and of oxygen and 0·5 mm. of argon.

Temperature coefficient. In Table VIII, 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 decomposition, yet the fact that the pressure of non-condensable gas ($p_{tot.} - p_{PH_3}$) decreases a little, shows quite definitely that there is very little decomposition accompanying oxidation.

FIG. 3.



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. Finally, owing to the fact that phosphine raises the lower oxidation limit of explosion of phosphorus–oxygen mixtures (Melville, *Trans. Faraday Soc.*, 1932, **28**, 314), 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 phosphorus–oxygen chains, the same molecule might provide centres for the phosphine reaction. There was, however, no acceleration of the reaction; indeed, a slight retardation was found. The pressure of phosphorus vapour did not exceed 0·030 mm.

TABLE VIII.

(D = Decomposition; O = oxidation; E_D = 24·3 kg.-cals.; E_O = 21·8 kg.-cals.)

Temp., K.	931°.	879°.			833°.			768°.		
	D.	*D.*	*O.*		*D.*	*O.*		*D.*	*O.*	
t.	p_{PH_3}.	p_{PH_3}.	$p_{tot.}$.	p_{PH_3}.	p_{PH_3}.	$p_{tot.}$.	p_{PH_3}.	p_{PH_3}.	$p_{tot.}$.	p_{PH_3}.
0	0·399	0·401	0·794	0·399	0·400	0·795	0·399	0·404	0·788	0·397
1	0·328	0·328	0·699	0·310	0·370	0·716	0·332	—	0·755	0·371
2	0·263	0·263	0·621	0·239	—	0·659	0·279	0·398	0·726	0·351
4	0·158	0·273	0·527	0·153	0·313	0·576	0·201	0·382	0·672	0·302
8	—	0·174	—	—	0·251	0·467	0·092	0·362	0·592	0·230

Temp., K.	730°.			698°.	
	D.	*O.*		*O.*	
t.	p_{PH_3}.	$p_{tot.}$.	p_{PH_3}.	$p_{tot.}$.	p_{PH_3}.
0	0·395	0·804	0·412	0·795	0·401
2	—	0·775	0·401	0·774	0·382
4	0·385	0·749	0·381	0·756	0·371
8	0·375	0·719	0·352	0·731	0·357
16	0·361	0·657	0·310	0·690	0·325

A peculiar observation with regard to the deposition of red phosphorus was made after a number of oxidation experiments had been carried out. The walls of the reaction tube opposite 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 before) are apparently efficiently reflected from an HPO_2 surface but are relatively easily condensable on a silica surface.

DISCUSSION.

Since 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 appear that oxygen is unable to displace adsorbed phosphine. 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 indicates the production of HPO_2, the simplest mechanism which may be postulated is the following : Phosphine is decomposed step by step on the molybdenum surface, $Mo - PH_3 \longrightarrow Mo - PH_2 \longrightarrow Mo - PH \longrightarrow Mo - P$, the PH_2, PH, or P remaining strongly adsorbed until there is reaction between adjacent radicals to yield P_2 and H_2, which evaporate. During the progress of this series of reactions, an oxygen 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 phosphine is decomposed directly into its elements; on the other hand, if this pressure 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 phosphoric acid. It may be that it will then be necessary for two oxygen molecules to collide in close proximity to one phosphine molecule in order to effect this oxidation, in which 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; but 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 adsorbed 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_{O_2} is much less than p_{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 reaction cannot induce reaction in phosphine–oxygen mixtures. In this case, of course, the ejection of carriers 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 intermediate products of dissociation, which are undoubtedly reactive and suitable for chain propagation, as is shown by the photochemical experiments, are so strongly adsorbed to 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 able to escape from the surface. In the latter reaction, on the other hand, the only intermediate product is probably P_2 (the filament is hardly hot enough for phosphorus atoms to be present in any quantity; compare Preuner and Brockmoller, *Z. physikal. Chem.*, 1913, **81**, 159), which can be easily and quickly desorbed from the surface before the arrival of oxygen 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 the concentration of phosphorus vapour, shows that adsorption is very strong. An oxygen molecule has therefore a good opportunity of reacting with adsorbed phosphorus.

It has been shown (Fig. 3) 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 $E_O > E_D$, that (*a*) at temperatures higher than 836° K., the rate of oxidation would become very much greater than the decomposition, (*b*) at temperatures less than 836° K., the decomposition would become the preponderant reaction and the oxygen would be without effect. It is remarkable that for tungsten $E_O \doteqdot E_D$.

The Effect of Atomic Hydrogen on the Catalytic Decomposition of Phosphine and Ammonia.

In the photochemical experiments on the decomposition of phosphine, it was shown that atomic hydrogen can react with the transitory intermediate products of the dissociated molecule to re-form phosphine; similar effects were obtained with ammonia (Melville, *Trans. Faraday Soc.*, 1932, **28**, 885).* It was suggested that the inhibition was due to the reaction $H + PH_2(NH_2) \longrightarrow PH_3(NH_3)$, occurring at the walls of the reaction tube. If the decomposition of these molecules on the surface of a filament takes place in stages with the production of surface compounds of the nature W–PH_2 or W–PH, then it should be possible, in principle, to bombard the filament upon which phosphine or ammonia is being dissociated and so retard the rate of decomposition. The result of such an experiment is a little difficult to interpret for phosphine since there is the possibility of the reduction of the phosphorus in the gas or at the walls before condensation to the red modification.

The experimental procedure was similar to that employed in the photochemical experiments, the atomic hydrogen being produced by collision of the gas with an optically excited mercury atom. The reaction tube in Fig. 1 of the first paper (*loc. cit.*) was replaced by one of silica 2·5 cm. in diameter, whilst the filament assembly remained the same. It was not possible to use the oil manometer with ammonia as this gas dissolved very rapidly in the oil; nor could nickel be used for phosphine owing to disintegration of the filament.

TABLE IX.

Gas.	Filament and conditions.*	Time of expt.	p_X.†	p_{H_2}.	Δp_X.
PH_3.	Mo; *L*	5	0·286	0·636	0·124
	L+F	5	0·292	0·636	0·189 (0·472)
	F	5	0·295	0·633	0·248
NH_3	Mo; *F*	2	2·06	4·06	1·44
	L	2	1·83	4·20	0·00
	L+F	2	1·83	4·20	0·90
PH_3	Mo; *F*	2	1·92	5·58	1·62
	F+L	2	1·92	5·38	1·14 (1·69)
	L	2	1·77	5·88	0·07
NH_3	W; *L*	2	1·93	4·02	0·01
	F	2	1·55	3·93	0·78
	F+L	2	1·91	3·72	0·56 (0·79)
PH_3	W; *L*	2	1·84	3·66	0·87 (0·93)
	F	2	1·91	3·59	0·09
	F+L	2	1·96	3·60	0·84
NH_3	Ni; *F*	2	1·87	3·74	0·29
	F+L	2	1·95	3·57	0·15
	L	2	1·95	3·57	0·00
PH_3	W; *L+F*	4	0·278	0·582	0·153 (0·234)
	L	4	0·298	0·580	0·048
	F	4	0·283	0·582	0·186
	L	4	0·308	—	0·111

* *L* = Lamp, *F* = filament. The figures in parentheses refer to the amount of gas decomposed by the lamp and the filament when used separately. † $p_X = p_{NH_3}$ or p_{PH_3}.

An inspection of the results (Table IX) shows that in every case the amount of gas decomposed by the filament and lamp simultaneously is less than that when these agents are

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* The results with ammonia have been confirmed and extended by Dr. L. Farkas, using the velocity of the change $H_{2(para)} \longrightarrow H_{2(ortho)}$ to measure the concentration of atomic hydrogen (private communication).

operated separately; *i.e.*, the simultaneous production of atomic hydrogen with the dissociation of ammonia or phosphine leads to a retardation of the latter process. This result is almost to be expected for ammonia, as molecular hydrogen is an inhibitor for the decomposition. The dissociation of hydrogen no doubt facilitates adsorption, for it virtually removes the necessity of activation which is required when a normal hydrogen molecule collides with the catalyst. The inhibition must occur 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 (Frankenburger and Hodler, *Trans. Faraday Soc.*, 1932, **28**, 229, and subsequent papers in *Z. Elektrochem.*).

That a similar mechanism holds for phosphine is probable from the following argument. If a mixture of phosphorus and mercury vapours is illuminated by a mercury lamp, there is a deposition of red phosphorus. The P_4 molecules are therefore changed in some way so that they undergo the allotropic transformation. If hydrogen is present also, no appreciable amount of phosphine is produced, *i.e.*, 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 to yield phosphine. The retardation observed is therefore likely to have taken place on the surface of the filament itself, as in the ammonia reaction. It is surprising, in view of the similarity in the behaviour of atomic hydrogen with respect to ammonia and phosphine, that in the latter case inhibition by molecular hydrogen is absent.

SUMMARY.

The kinetics of the oxidation of phosphine on molybdenum and tungsten filaments at pressures below the lower explosion limit have been investigated in order to determine whether a hot filament might induce the homogeneous combination of the gases, as is the case with phosphorus–oxygen mixtures. No measurable amount of homogeneous reaction could be detected, the reaction taking place almost wholly on the surface; a faint glow accompanied the oxidation, however, thus providing evidence of a trace of homogeneous reaction. Experiments with a silica and with a Pyrex filament were also unsuccessful. The presence of phosphorus does not induce the reaction to come off the surface.

A theory is proposed to account for the differences in the reactions of oxygen with phosphine and with phosphorus.

Experiments are described in which the catalytic decomposition of phosphine and ammonia is inhibited by the simultaneous bombardment of the filament by atomic hydrogen.

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