147. *The Thermal Decomposition of Phosphine by Tungsten and Molybdenum.*

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RECENT investigations on the kinetics of thermal chain reactions have emphasised the fact that surfaces are responsible not only for the termination of chains but also for their initiation (cf. Hinshelwood, *Trans. Faraday Soc.*, 1932, **28**, 184). The latter effect extends to the explosive reaction and to the stable chain reaction, which occurs, in some cases, in the region outside the explosion limits. Whilst the kinetics of explosions have been satisfactorily worked out, in a general manner, notably by Hinshelwood and by Semenoff, the investigation of possible stable chain processes is more likely to lead to a better understanding of the mechanism, as a wider variety of conditions for reaction can be studied and also more easily controlled.

A chain reaction consists essentially of three distinct phenomena, *viz.*, (*a*) initiation, (*b*) propagation, (*c*) termination of the chain. In order to investigate the kinetics of the reaction in detail, some means are required to separate these processes. Since the starting of chains depends upon the introduction of reactive molecules or atoms into the gas mixture, a variety of ways exists whereby initiation may be induced. It has been shown (Melville and Ludlam, *Proc. Roy. Soc.*, 1932, *A*, **135**, 315) that in the oxidation of phosphorus a hot tungsten, molybdenum, or glass filament is capable of initiating a stable chain reaction below the lower limit. This reaction has many of the chain characteristics of the explosive reaction at the lower limit (Semenoff, *Z. Physik*, 1927, **46**, 109). By the use of a hot filament, then, a method is available in certain circumstances whereby the initiation of chains may be accurately controlled, provided that the mixture be in a condition to propagate chains once they have been started.

The kinetics of the oxidation of phosphine and of phosphorus are very similar. Further, it has been shown (Melville, *Proc. Roy. Soc.*, 1932, *A*, **138**, 374; 1933, *A*, **139**, 541) that a stable chain reaction may be started by excited mercury atoms or by the direct photochemical decomposition of the phosphine molecule. The photochemical experiments have also indicated a chain length very nearly equal to that calculated on the assumption that reaction occurs at every collision between chain carriers and reactant molecules. Phosphine–oxygen mixtures below the lower explosion limit are therefore capable of propagating chains with suitable primary stimulation.

FIG. 1.

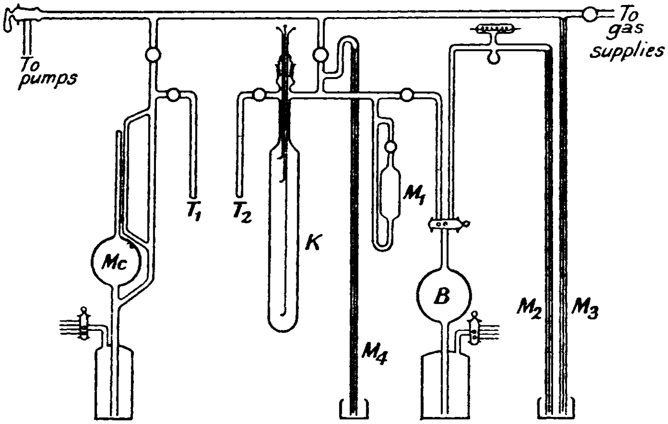
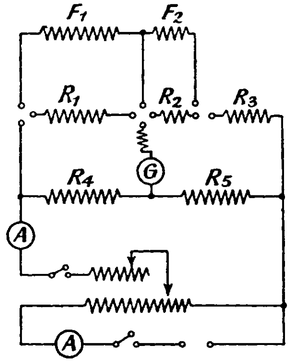


FIG. 2.



It was consequently anticipated that the oxidation of phosphine, like that of phosphorus, might be induced by hot filaments. Before such an investigation could be carried out, it was necessary to study the kinetics of the decomposition of phosphine on tungsten and molybdenum filaments. The present paper is concerned with this aspect of the problem, and the oxidation will be dealt with in another communication.

EXPERIMENTAL.

Preparation of Gases.—PH_3 was prepared by dropping KOH aq. on PH_4I, passing the PH_3 evolved over NaOH, $CaCl_2$, and P_2O_5, and collecting in a liquid-air trap. The PH_3 was then subjected to fractional distillation. The H, O, and A were taken from cylinders and purified by the usual methods, all gases being dried with P_2O_5.

Apparatus.—The essential parts of the apparatus are shown diagrammatically in Fig. 1. The reaction tube (*K*) was 3 cm. wide and about 20 cm. long. This was surrounded by a water-bath maintained at a const. temp. (usually about 20°). *K* was exhausted by a Hg condensation pump backed by a Hyvac oil pump. In addition to the gas reservoirs and pipettes, suitable side tubes cooled in liquid air were connected to the apparatus in order to facilitate the analysis of gas mixtures containing PH_3. A small Topler pump (*B*) was used for transferring gas in *K* to a tube containing a Pt wire for analysing the H–O mixtures obtained in the oxidation expts.

Several types of pressure gauge were employed. For the lowest pressures, a McLeod gauge (M_2) was most convenient, but for somewhat higher pressures a glass spring manometer was used. Later expts. were made with an oil manometer (M_1). The right (exhausted) limb was of much wider tubing (2·5 cm. diam.) than the left limb (0·4 cm.), 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. $< 10^{-7}$ mm. Hg proved to be suitable, as it did not appreciably dissolve the gases which were used in these expts. The oil was thoroughly degassed before use by warming in a vac. A sensitivity of 0·001 mm. was easily reached by using a microscope to read the position of the oil. M_2, M_3, and M_4 were capillary Hg manometers. Apiezon grease " L " was used as a tap lubricant.

Determination of Filament Temperature.—In order to eliminate, as far as possible, end losses, the filament was constructed in an unusual manner. Preliminary expts. had shown that the rate of decomp. of the PH_3 was conveniently measurable at temps. 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 (Langmuir, MacLane, and Blodgett, *Physical Rev.*, 1930, **35**, 478).

The principle of this new method is as follows. Two filaments, one 3—4 times longer than the 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 " resistance of the two filaments. The rate of reaction on the filament minus the rate on the small filament is therefore the rate due to a central portion of the large filament which is at an approx. const. temp. throughout its length. Similarly, the difference in resistances of the two filaments gives the resistance of this central portion, and from the resistance–temp. relation of the metal, the mean temp. of the central portion can be accurately calculated. To ensure that the filaments did run under precisely identical conditions, each formed the arm of a Wheatstone bridge, in which circumstances small losses in the connecting leads were simultaneously balanced out.

The filament was spot-welded to 1 mm. Ni leads, " copper clad " wire being used to make the metal–glass seals. The electrical connexions are shown in Fig. 2. F_1 and F_2 denote the large and the small filament respectively, whilst R_1 and R_2 are variable resistances whereby F_1 or F_2 can be balanced out; R_3 is a fixed resistance. R_1, R_2, and R_3 were all made of constantan wire of such a diameter as to carry the bridge current without appreciably changing in resistance. R_4 and R_5 are much higher resistances (*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 on the W or the Mo filament a deposit of red P is formed on the walls of the tube containing the filament. The density of distribution of this deposit, when the decomp. was carried out at low press., indicated approx. the effective length of the filament. For a 12-cm. filament, this length was found to be *ca.* 9 cm. at the temps. used in these expts. The small filament was therefore made 3 cm. long.

With F_1 and F_2 in circuit, suitable temp. and press. ranges were found, and the bridge was balanced by the adjustment of R_5. A run was then made, and the velocity calculated according to the methods described below. With the same press. of PH_3, another run was carried out, R_1 being substituted for F_1. The rate due to F_2 was thus obtained, and by subtraction the rate due to the central portion of F_1. R_1, R_2, R_3, R_4, and R_5 were all known, so the resistance of F_1 and of F_2 could easily be calculated.

If for any reason the temp. of the filament was changed, the above balancing was repeated. In the comparatively small temp. range which could be conveniently used, it was unnecessary to find the reaction velocity due to each filament at the several temps. used. A small correction —4%—was applied to the rate of reaction with both filaments in circuit in order to reduce this rate to that due to the central portion of the large filament. The bridge currents, with 0·1 mm. diam. wires, ranged from 0·3 to 1·5 amp. On each occasion in which a new filament was put into use it was subjected to a thorough out-gassing for several hr. under 10^{-5} mm. The resistance–temp. curves for each specimen of wire were separately determined.

Although W and Mo were used entirely in these expts., one or two runs were made with Ni and with a Ni–Fe alloy. The temp. to which these required to be heated was approx. the same as that for W and Mo, but they did not survive more than one or two expts. involving the decomp. of about 5 mm. PH_3 in a vol. of 200 c.c. The P appeared to attack the metal, rendering it very brittle and finally causing its complete disintegration, presumably owing to formation of a phosphide. Mo and W 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 press. increase during the decomp. which must be due to H, but the question arises as to whether all of the H is liberated into the gas phase. Exptl. data given below support the view that the decomp. can be represented by the equation $4PH_3 = P_4$(red) $+ 6H_2$, no appreciable proportion of P_2H_4 or any of the solid hydrides of P being formed.

What is more important, from the point of view of possible chain-initiator molecules, is the mechanism of the formation of the P. Although a red deposit appears on the walls of the reaction tube, P vapour may also be produced. There are, therefore, two possible end states in which P might occur: (1) a mixture of red P, white P, and P vapour; (2) red P entirely. Another possibility is the intermediate formation of P_4 or of white P, since normal P_4 mols. might evaporate off the filament, in the first instance, collide with the walls, and eventually return to the filament, whereby they are altered in some manner so that on colliding with the walls again red P is formed. The formation of red P from P vapour (P_4 mols.) has been repeatedly observed in a tube containing a W or Mo filament sufficiently hot to decompose PH_3.

To decide the matter, the following expt. was made, which was typical of many. 0·92 Mm. of PH_3 was admitted to the reaction tube, which was surrounded by a CO_2–Et_2O bath at − 80°. The filament was heated until there was no further press. change; the press. increase was 0·46 mm., thus confirming the equation given above. The H was pumped off and the bath withdrawn to allow any white P to evaporate. 0·63 Mm. of O was added, but no glow could be observed, nor was there any observable press. change. The absence of glow indicated that the press. of P_4 was less than 2×10^{-3} mm., which is the p_{P_4} at the lower explosion limit with 0·6 mm. of O in a 2 cm. tube. No appreciable amount of P vapour was thus formed. Had the P evaporated from the filament as normal P_4 mols., these would have condensed on the cool glass surface and re-evaporated when the reaction tube was warmed to room temp. This expt. also provides evidence that there is no intermediate formation of white P, or of P vapour. The P must therefore leave the filament in such a form that it condenses on the surface, is adsorbed, and ultimately forms red P. It has been shown (Melville, *Proc. Roy. Soc.*, 1932, *A*, **138**, 394) that P_2 mols. polymerise to red P on hitting a glass surface, and therefore it is probable that the P leaves the filament as P_2 mols.

Another confirmatory experiment was made. 6 Mm. of PH_3, occupying 200 c.c., gave a film of red P which just exhibited interference colours. The film was 10 cm. long and the diameter of the tube 2 cm., so that it would require at least 3×10^{-3} g. of red P to form such a film, whereas 200 c.c. of PH_3 at 6 mm. would yield $2{\cdot}4 \times 10^{-3}$ g. of P on being decomposed.

A curious effect was noticed during this work. Although the film of red P was usually of uniform thickness, in some instances, patches of the reaction tube remained only slightly covered, whilst in other parts the deposit was dense. It would appear that the walls exert a definite activity towards the deposition of red P. It is of interest, therefore, that, not only is the combination of atoms on a wall dependent on its nature, but, in this case, the polymerisation of mols. is likewise affected. No expts. have been carried out with walls of different materials, but the reaction tubes were cleaned with Br aq. to remove red P and were subsequently washed out with H_2O and dried.

As these expts. are preliminary to the study of the oxidation at press. below the lower explosion limit, the press. of PH_3 used ranged from a few mm. down to the lowest press. which could be measured on the McLeod gauge. The general procedure (at higher press.) was to admit PH_3, note its press., switch on the filament current, and take press. readings at convenient time intervals. Upon heating the filament, however, there is a small press. increase due to heating of the gas. A correction has to be applied to the observed press. in order to find the true value at the temp. of the walls of the reaction tube; this was measured by filling the reaction tube with O and finding the press. increase on heating the filament to the temp. at which it was to be subsequently employed. This procedure was repeated for different press. O has nearly the same thermal conductivity as PH_3 and does not react with filament at the temp. used for the decomp. of PH_3. A similar series of expts. was made with H. As the correction for O was only double that for H, 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 PH_3–H mixture as the H accumulates during the reaction. For a 1 : 1 mixture, therefore, the correction factor is the mean of that for PH_3 and for H alone.

A typical series of press.–time observations at a number of different initial PH_3 press. is given in Table I, $t_{\frac{1}{2}}$ being the time of half-decomp. All press. are in mm. Hg, and times (t) in min.; col. 2 ($p_{PH_3+H_2}$) is the actual obs. press., Δp is the press. increase corrected for the small heating effect.

TABLE I.

Length of Mo filament, 14·9 cm.; diam. of filament, 0·01 cm.; temp. of filament, 464°; vol. of reaction tube, 90 c.c.; temp. of reaction tube, 20°.

Expt. 59.

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

Δp_∞ 0·34
$t_{\frac{1}{2}}$ = 2·4 min.

Expt. 60.

t.	$p_{PH_3+H_2}$.	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

Δp_∞ 0·58
$t_{\frac{1}{2}}$ = 3·6 min.

Expt. 61.

t.	$p_{PH_3+H_2}$.	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

Δp_∞ 1·00
$t_{\frac{1}{2}}$ = 6·0 min.

Expt. 62.

t.	$p_{PH_3+H_2}$.	Δp.	$\Delta p/t$.
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

Δp_∞ 1·37
$t_{\frac{1}{2}}$ = 8·0 min.

Expt. 63.

t.	$p_{PH_3+PH_2}$.	Δp.	$\Delta p/t$.
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

Δp_∞ 1·79
$t_{\frac{1}{2}}$ = 9·5 min.

The first characteristic of these expts. is that the time required for half-decomp. increases with the press. of the PH_3. Similarly, the initial rate of reaction is maintained and does not decrease until a large fraction of the PH_3 is decomposed. Further, the initial rate only increases 50% for a press. increase from 0·67 to 3·58 mm. PH_3.

The effect of H was next investigated to find whether it might modify the course of the decomp. as it accumulates in the system: no influence could be measured, the half-life being independent of H press., as is shown by the following two series of results:

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

It may be concluded, therefore, that at pressures of the order of a few mm. of Hg, the course of the decomp. conforms nearly to a reaction of zero order.

Low-pressure Experiments.—The deviations of the above results from a zero-order reaction suggested that at lower press., adsorption of PH_3 might be so much less marked that the reaction would become unimol. The expts. were made with the McLeod gauge as manometer, and consequently the procedure had to be slightly modified. PH_3 to the required press. was passed into the reaction system and the filament switched on for a given time, after which the total press. was determined. This was repeated until practically all the PH_3 was decomposed. Conditions were arranged so that the time required to heat the filament to its working temp. was about 1% of the time of reaction. The vol. of the McLeod gauge and connexions was determined, so the obs. reaction velocity could be reduced to the value obtaining in the reaction tube used in the high-press. expts.

Table II gives a typical series of runs using the same filament temp. as in Table I; k is the unimol. coeff., $1/t \,.\, \log_{10} a/(a - x)$, where a is the initial press. of PH_3 and x that of decomposed PH_3. The vol. of the apparatus was 390 c.c.

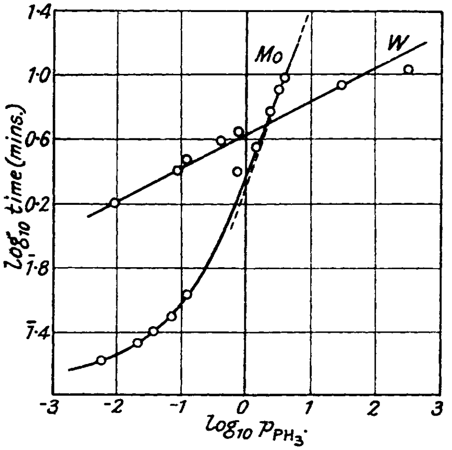
TABLE II.

t.	$p_{PH_3+H_2}$.	Δp.	k.	$\Delta p/t$.	t.	$p_{PH_3+H_2}$.	Δp.	k.	$\Delta p/t$.
		Expt. 67.					Expt. 68.		
0	0·1240	0	—	—	0	0·0695	0	—	—
1	0·1450	0·0210	0·178	0·021	1	0·0845	0·0150	0·246	0·0150
2	0·1585	0·0345	0·176	0·0173	2	0·0925	0·0230	0·236	0·0115
3	0·1690	0·0450	0·180	0·0150	3	0·0970	0·0275	0·227	0·0092
4	0·1755	0·0515	0·193	0·0129	4	0·0985	0·0290	0·196	0·0072
6	0·1825	0·0585	0·209	0·0098	6	0·1000	0·0305	0·133	0·0051
8	0·1835	0·0595	—	0·0074	8	0·1115	0·0320	0·146	0·0040
		Δp_∞ 0·0620					Δp_∞ 0·0347		
		$t_{\frac{1}{2}}$ 1·8 min.; $t'_{\frac{1}{2}}$ 0·42 min.*					$t_{\frac{1}{2}}$ 1·35 min.; $t'_{\frac{1}{2}}$ 0·313 min.		
		Expt. 69.					Expt. 70.		
0	0·0385	—	—	—	0	0·0190	—	—	—
1	0·0490	0·0105	0·342	0·0105	1	0·0235	0·0445	0·278	0·0045
2	0·0520	0·0135	0·263	0·0067	2	0·0270	0·0080	0·217	0·0040
3	0·0550	0·0165	0·282	0·0055	3	0·0275	0·0085	0·328	0·0028
4	0·0565	0·0180	0·297	0·0045	4	0·0277	0·0087	0·259	0·0022
		$t_{\frac{1}{2}}$ 1·08 min.; $t'_{\frac{1}{2}}$ 0·251 min.					Δp_∞ 0·0095		
							$t_{\frac{1}{2}}$ 0·95 min.; $t'_{\frac{1}{2}}$ 0·220 min.		
				Expt. 71.					
0	0·0060	0	—	—	3	0·0087	0·0027	0·33	0·0009
1	0·0080	0·0020	0·176	0·0020	4	0·0087	0·0027	—	0·0007
2	0·0085	0·0025	0·38	0·0013			$t_{\frac{1}{2}}$ 0·70 min.; $t'_{\frac{1}{2}}$ 0·162 min.		

* $t'_{\frac{1}{2}}$ is the value $t_{\frac{1}{2}}$ would have in a reaction vessel of the vol. used in the high-pressure expt.

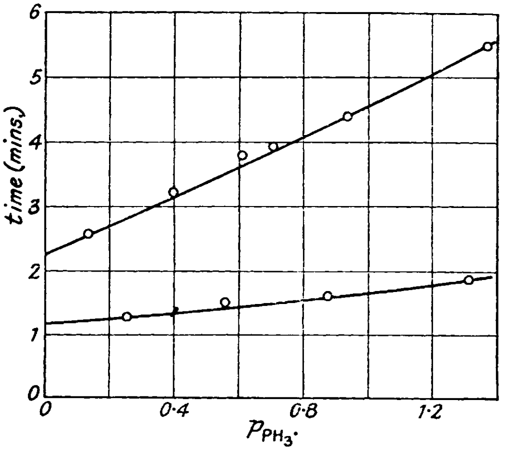
Even at quite low press., the time required for half-decomp. is slightly dependent on press., but the approx. constancy of the values in col. 4 of Table II indicates that the reaction is very nearly unimol. The value of $\Delta p/t$ drifts considerably, as is to be expected.

FIG. 3.



The $\log_{10}$ *of time for half decomposition* (Mo) *and for quarter decomposition* (W) *of* PH_3 *plotted against* $\log_{10} p_{PH_3}$. *The broken line on the* Mo *curve represents a zero-order reaction. Temp. of* Mo *filament* 464° *and of* W *filament* 560°.

FIG. 4.



The time for half decomposition of PH_3 *on* Mo *filament at* 570° *and* 645° *plotted against* p_{PH_3}.

If the reaction is of zero order, then on plotting log t against log p a straight line of unit slope should be obtained, whereas a unimol. reaction would give a line parallel to the log p axis since t is independent of press. Such a plot has been made in Fig. 3 from the results in Tables I and II and some additional results not recorded. At higher press., 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 press. since the half-life period would have been several hours. On the other hand, had the reaction rate been increased by raising the temp. of the filament, the order would have risen owing to evaporation of adsorbed PH_3, and consequently a much higher press. would be required to approach the zero-order reaction.

Temperature Coefficient.—The measurement of the temp. coeff. 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 Mo surface can be calculated from the variation of $t_{\frac{1}{2}}$ with temp. by means of the formula $d \log (1/t_{\frac{1}{2}})/dT = E/RT$. The apparent energy of activation (Q) of the unimol. reaction is composed of two terms (see, *e.g.*, Hinshelwood, " Kinetics of Chemical Change in Gases," 2nd Edn., p. 228) : the energy of activation (E) on the surface minus the heat of desorption (λ) of adsorbed PH_3. Since Q is easily measured, λ can be calculated. In the transition reaction Q will vary between those limiting values. It has been seen that at the low press. of 0·005 mm. the reaction is not quite of the first order; hence, in determining the temp. coeff. two sets of expts. were made. In the first, the temp. of the filament was maintained const., the variation of half-life with press. plotted, and the curve extrapolated to zero press. Another similar series of observations was made for another temp., and the results extrapolated to $p_{PH_3} = 0$. The ratio of $t_{\frac{1}{2}}$ for the two temps. for $p_{PH_3} = 0$ was used to calculate Q.

Table III contains the data for this calculation, and Fig. 4 shows $t_{\frac{1}{2}}$ plotted against p_{PH_3}.

TABLE III.

Temp. of reaction tube 20°.

Values of $p_{PH_3+H_2}$.

	Temp. of filament 645°.					Temp. of filament 574°.						
t.	Expt. 73.	Expt. 74.	Expt. 75.	Expt. 76.	Expt. 77.	Expt. 78.	Expt. 79.	Expt. 80.	Expt. 81.	Expt. 82.	Expt. 83.	Expt. 84.
0	0·0255	0·0445	0·1310	0·0580	0·0865	0·0610	0·0955	0·1365	0·0410	0·0117	0·0130	0·1090
1	0·0330	0·0515	0·1515	0·0685	0·1040	0·0660	0·1030	0·1465	0·0455	0·0133	0·0157	0·1145
2	0·0347	0·0575	0·1650	0·0775	0·1120	0·0695	0·1075	0·1515	0·0485	0·0157	0·0160	0·1175
3	0·0367	0·0605	0·1770	0·0805	0·1200	0·0735	0·1120	0·1585	0·0515	0·0160	0·0173	0·1220
4	0·0375	0·0635	0·1850	0·0845	0·1255	0·0760	0·1175	0·1625	0·0525	0·0163	0·0187	0·1265
5	—	0·0650	0·1915	0·0855	0·1270	0·0805	0·1215	0·1700	0·0540	—	—	0·1275
6	—	—	—	—	—	0·0810	0·1255	0·1735	—	—	—	0·1310
7	—	—	—	—	—	—	0·1280	0·1815	—	—	—	—

In expt. 84, 0·0385 mm. of H was present initially, and as seen from Fig. 4, $t_{\frac{1}{2}}$ lies on the curve, so H has no effect on the low-press. decomp.

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

p_{PH_3}	0	0·02	0·06	0·10	0·20
R_1/R_2	2·00	2·24	2·61	2·79	2·80
Q (kg.-cal.)	15·1	17·5	20·8	22·3	22·3

Fig. 3 shows that at the lower temp., the reaction is not unimol., whereas at the higher temp., where PH_3 is much less strongly adsorbed, unimol. characteristics are more closely obeyed, *i.e.*, $t_{\frac{1}{2}}$ is nearly independent of p_{PH_3}.

Measurements of the temp. coeff. were also made at higher press. with the results given in Table IV.

TABLE IV.

Temp. of reaction tube 17°. Vol. of apparatus and filament as in Table I.

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

Energy of activation $E = 39{\cdot}3$ kg.-cal.

The heat of desorption of the PH_3 is thus $39{\cdot}3 - 15{\cdot}1 = 24{\cdot}2$ kg.-cal. As this value is essentially calculated by extrapolation of the low-press. results to zero press., it represents the heat of desorption of the PH_3 from an uncovered surface of Mo.

Tungsten Filament.

W did not behave in the same way as Mo. The press. increase accompanying the complete decomp. was, however, exactly half the initial press. of PH_3. Similarly P was deposited as the red variety on the walls of the tube. On carrying out expts. similar to those with the Mo filament to determine whether white P was an intermediate product, some traces of it were found; *e.g.*, in one expt., after the PH_3 (*ca.* 0·5 mm.) had been decomposed and the reaction tube pumped out, on admission of a few mm. of O there was a bright flash of about 1 sec. duration. There was no succeeding continuous glow and no change of press. The amount of white P produced by the filament was estimated to be less than 0·05 mm.

TABLE V.

Temp. of W filament, 560°; length of long filament, 12·0 cm.; length of short filament, 3·0 cm.

t.	$p_{PH_3+H_2}$.	p_{PH_3}.	k.	t.	$p_{PH_3+H_2}$.	p_{PH_3}.	k.	t.	$p_{PH_3+H_2}$.	p_{PH_3}.	k.
	Expt. 256.				Expt. 257.				Expt. 260.		
	Vol. 324 c.c.				Vol. 581 c.c.				Vol. 581 c.c.		
0	0·967	0·967	—	0	0·00855	—	—	0	0·1122	—	—
1	0·985	0·910	0·0262	1	0·00860	0·00845	—	1	0·1148	0·1070	0·022
2	1·003	0·875	0·0220	2	0·00915	0·00735	0·033	2	0·1183	0·1000	0·025
4	1·037	0·809	0·0195	4	0·00980	0·00585	0·041	4	0·1225	0·0916	0·022
8	1·100	0·701	0·0180	8	0·01080	0·00405	0·040	8	0·1303	0·0760	0·021
	$t/4$ = 6·2 min.				$t/4$ = 2·8 min.; $t'/4$ = 1·6 min.				$t/4$ = 5·6 min.; $t'/4$ = 3·1 min.		
	Expt. 261.				Expt. 271.				Expt. 275.		
	Vol. 581 c.c.				Vol. 121 c.c.				Vol. 121 c.c.		
0	0·0412	—	—	0	29·0	—	—	0	262·5	—	—
1	0·0434	0·0368	0·049	1	30·3	26·4	0·041	1	276·0	235·5	0·047
2	0·0453	0·0330	0·048	2	31·2	24·6	0·035	2	283·0	221·5	0·037
4	0·0472	0·0292	0·038	4	33·3	20·4	0·038	4	294·0	199·5	0·033
8	0·0505	0·0226	0·033	8	37·0	13·0	0·043	8	311·5	164·5	0·025
	$t/4$ = 2·9 min.; $t'/4$ = 1·65 min.				$t/4$ = 3·4 min.; $t'/4$ = 9·1 min.				$t/4$ = 4 min.; $t'/4$ = 10·7 min.		
	Expt. 278.				Expt. 279.				Expt. 280.		
	Vol. 121 c.c.				Vol. 121 c.c.				Vol. 121 c.c.		
0	0·795	—	—	0	0·396	—	—	0	0·099	—	—
1	0·854	0·677	0·070	1	0·429	0·330	0·080	1	0·111	0·075	0·120
2	0·904	0·577	0·070	2	0·458	0·272	0·082	2	0·117	0·063	0·098
4	0·989	0·407	0·073	4	0·504	0·180	0·085	4	0·130	0·038	0·104
8	1·102	0·181	0·080	8	0·558	0·072	0·092	8	0·140	0·018	0·092
	$t/4$ = 1·7 min.; $t'/4$ = 4·5 min.				$t/4$ = 1·5 min.; $t'/4$ = 4·0 min.				$t/4$ = 1·0 min.; $t'/4$ = 2·6 min.		

In Table V the results of a series of runs are given in which the press. was varied from 0·008 to 262 mm. The vol. 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 expt. $t'/4$ is the value $t/4$ would have in an apparatus of 324 c.c. The obs. reaction velocity is due to the two filaments. In order to calculate the rate produced by the central portion of the long filament, $t/4$ must be increased by 4%. k is the unimol. velocity coeff. as in Table II.

First, it is noteworthy that $t/4$ does not markedly depend on press. A 30,000-fold press. increase changes $t/4$ by less than a factor of 10, *viz.*, from 1·6 to 10·7 min. The reaction is therefore nearly unimolecular, as is further shown by the constancy of k in each run. Further, expts. were made with a press. of added H of the same order as that of the PH_3, but no inhibitory action was noticed either at high or at low press.

In Table VI are given two series of results with different filament temps., and at high (3 mm.) and low (0·05 mm.) press. The energies of activation (Q) are practically identical and therefore

TABLE VI.

Half-life (sec.).	Temp. of filament. (1).	(2).	Half-life (sec.).	Temp. of filament. (1).	(2).
120	560°	441°	192	523°	407°
240	523	407	492	482	359
720	482	359	96	560	447
3000	415	—			

Q = 25·8 kg.-cal. Q = 23·8 kg.-cal.

in agreement with the fact that the reaction is unimolecular over this range of press. The temps. given in col. 3 were calculated by the old method of measuring the resistance and assuming a uniform temp. along the filament; those calculated by the new method are materially higher. The wide discrepancy is shown more clearly by a calcn. of the value of Q. The first and third results of the low-press. expts. give $Q = 28{\cdot}7$ kg.-cal., whereas the lower temp. gives $Q = 18{\cdot}7$ kg.-cal. Although the abs. value of the temp. and energy of activation of the reaction of the surfaces of filaments is not at present of great theoretical importance, yet the discrepancy may alter the significance of any theoretical discussions in comparing similar reactions catalysed by filaments of different materials.

DISCUSSION.

The results may be summarised as follows. At low pressures, *i.e.*, less than 0·1 mm., phosphine decomposes according to a unimolecular law on tungsten and on molybdenum; the rate of reaction is unaffected by the presence of molecular hydrogen. No inhibitory influence of phosphorus can be detected for the simple reason that as soon as it leaves the filament it is removed from further possible action by condensation on the walls of the reaction tube. Further, the activities of the two catalysts appear to be of the same order of magnitude. As the pressure of the phosphine is increased, 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. In neither case is there any influence of hydrogen.

At the comparatively low temperatures at which these wires function, it is improbable that the evaporating hydrogen is anything but normal molecules, possessing an energy of translation 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. It is otherwise with the phosphorus. When P_4 molecules derived from white phosphorus condense on a cool surface, they do not in general condense to the red modification. Hence the molecules of phosphorus which evaporate from the filament cannot be normal P_4 molecules.

In a previous paper (Melville, *Proc. Roy. Soc.*, 1932, *A*, **138**, 394) mention has been made of an experiment in which normal P_4 molecules at low pressure are passed through a fine silica jet at 700° so as to dissociate them into P_2 molecules. That such molecules are actually formed by heating phosphorus vapour is shown, not only by density measurements (Preuner and Brockmoller, *Z. physikal. Chem.*, 1931, **81**, 159), but also by the appearance of an absorption band spectrum corresponding to P_2 molecules (Jakolewa, *Z. Physik*, 1931, **69**, 548). A second cool jet defines a molecular beam which is projected into an evacuated tube provided at one end with a cool surface at − 80°. Condensation of the P_2 molecules gives rise to a red deposit. Now the temperature of the filaments in these experiments is sufficient to dissociate P_4 molecules. Further, in the experiments on the initiation of chains in phosphorus–oxygen mixtures by hot wires, it was observed that mere heating of a tungsten or molybdenum wire to 500° in phosphorus vapour produced a deposit of red phosphorus in the reaction tube. It may be concluded, therefore, in absence of evidence to the contrary, that P_2 molecules evaporate from a filament upon which phosphine molecules are being dissociated. The question then arises as to whether these P_2 molecules can initiate a chain reaction between phosphine and oxygen. This problem will be treated in a later paper.

There is, as might be expected, 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 catalysts must be raised in order to obtain a measurable rate of reaction is rather higher for it than for phosphine; *e.g.*, on tungsten, phosphine at 500° has a half-life period similar to that of ammonia at 1000°, as found by Kunsman (*J. Amer. Chem. Soc.*, 1928, **50**, 2100; *Phil. Mag.*, 1930, **10**, 1015) 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 $\lambda_{NH_3} > \lambda_{PH_3}$. At low pressures both reactions are unimolecular.

With molybdenum, 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, whereby the order of the reaction increases from zero to unity.

One important 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 at low pressures. If the surface of the catalyst is catalytically uniform and if the inhibitory effect of hydrogen on ammonia is merely due to displacement of adsorbed ammonia, then absence of inhibition by hydrogen on phosphine is not to be expected. There are two alternative explanations of this discrepancy : (*a*) the catalyst is not of uniform activity and the ammonia decomposes on centres which can be easily covered with hydrogen, whereas different active centres for phosphine are not affected by hydrogen ; (*b*) hydrogen not only displaces ammonia, but after or as a consequence of being adsorbed it becomes sufficiently reactive to attack the intermediate products of the decomposition of the ammonia molecule and to regenerate this gas. In the second case inhibition by hydrogen would then be due essentially to a chemical reaction, and therefore it is reasonable to suppose that there would be a marked difference in the condition for the appearance of inhibition.

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., which is much higher than the values for phosphine. Although, in general, there is no connexion between activity of catalyst and E, yet it happens that tungsten and molybdenum are much more active for phosphine than for ammonia, *i.e.*, increased activity is associated with a low energy of activation.

SUMMARY.

The decomposition of phosphine has been studied on the surface of tungsten and molybdenum filaments at pressures from 0·01 to 300 mm. Reaction velocity is measurable at about 500°. On tungsten, the order of the reaction is nearly unity and is not much affected by pressure. On molybdenum, the decomposition is unimolecular at low pressures but becomes of zero order as the pressure is increased. The heat of adsorption of the phosphine has been calculated from the temperature coefficient of the reaction at high and at low pressures. The products of the reaction are red phosphorus and hydrogen. Molecular hydrogen has no effect. These reactions have been compared with the corresponding ammonia reactions.

A simple method of correcting for end losses in a hot filament is described.

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