THE SLOW OXIDATION OF PHOSPHORUS.

by

Christina Cruickshank Miller, B.Sc., Ph.D.

Thesis for the Degree of D.Sc.

June 1929.

INDEX.

(Contd.)

THE SLOW OXIDATION OF PHOSPHORUS.

The element Phosphorus was prepared by Brandt[1] in the seventeenth century and was at once a source of special interest, owing, no doubt, to the fact that in air it gave a glow which was easily visible in the dark.   When oxygen was excluded, Davy and Berthollet[2] found that no luminosity occurred in the inert gases, hydrogen, nitrogen, carbon dioxide, etc. The luminescence was therefore the concomitant of an oxidation process, a conclusion which has been amply verified by the work of subsequent investigators.

Although oxygen is essential for the appearance of luminescence phosphorus does not glow in oxygen under all conditions.   Davy found that there was no glow in pure oxygen at 16°, and later Joubert[3] established the existence of a so-called "boundary pressure" of moist oxygen above which neither luminescence nor oxidation occurred.   Lord Rayleigh[4] has shown, however, that a slow absorption of oxygen takes place although no glow is visible.   Joubert further indicated that below a certain pressure of oxygen too small to measure phosphorus did not combine with oxygen.   That such a critical pressure of oxygen exists has been shown by Chariton and Walta[5] and, more conclusively, /

conclusively, by Semenoff[6]. Baker[7] found that in complete absence of moisture phosphorus neither glowed nor oxidised in oxygen.

Phosphorus glows more brightly in air or oxygen when the pressure is reduced, increasing brightness of the glow usually implying acceleration of the oxidation process. Ewan[8] and Russell[9], in particular, have studied the rate of oxidation of phosphorus in oxygen under various conditions.

The oxidation of phosphorus in presence of an excess of moisture was shown by Schönbein[10] to be accompanied by formation of ozone and hydrogen peroxide, but no ozone was produced if the oxygen was dried with concentrated sulphuric acid. Russell obtained the same result.

Moisture is also essential for the ionisation that usually accompanies the oxidation of phosphorus. According to Busse[11] it is caused by the dissociation of an acid, probably pyrophosphoric acid, formed in the course of the slow oxidation. Ionisation appears, however, to be a secondary feature of the oxidation as Harms[12] calculated that only one ion was produced in eight million reacting molecules.

Another striking feature in connection with the oxidation of phosphorus is the inhibition of the glow/

glow by very small quantities of certain vapours and gases. Thus Graham[13] found that at 25° one volume of ethylene in 450 volumes of air was sufficient to stop the glow. Emeléus[14] has shown, however, that a slow absorption of oxygen takes place even although glowing is prevented. Centnerszwer[15] has considerably extended Graham's work and studied the effect of varying the concentration of the inhibitors.

To sum up, the oxidation of phosphorus possesses the following interesting features — it exhibits chemiluminescence, but the glow is prevented and oxidation markedly retarded by a great many vapours and gases, including moist oxygen itself; oxidation in moist oxygen is accompanied by ionisation and the indirect formation of ozone and hydrogen peroxide. These phenomena have been investigated by a large number of chemists and physicists but so far no comprehensive theory has been advanced to embrace all of them.

The chemiluminescence exhibited by slowly oxidising phosphorus trioxide is interesting in connection with the oxidation of phosphorus. Thorpe and Tutton[16] who were the first to prepare this oxide in quantity and study its properties, found that its glow like that of phosphorus was brighter under diminished oxygen pressure. That /

That the glow might be due to the presence of free
phosphorus in the oxide was of course considered, but
the supposition was rejected as unlikely.

Some years later, Russell[9] in studying the
reaction between phosphorus and moderately dried oxy-
gen at high pressure found that it might be divided
into two stages.   In the first, oxidation was slow
and accompanied by a very feeble glow, but in the
second, when pressure had fallen below 500 mm. oxida-
tion was continuously accelerated until all of the oxy-
gen was absorbed.   The glow was very bright, and an
oxide formed in the first stage evidently oxidised
further in the second stage to phosphorus pentoxide.
Russell did not specify what the intermediate oxide
was.

Jungfleisch[17ab], however, definitely attribu-
ted the glow of phosphorus to the oxidation of phos-
phorus trioxide which he believed to be formed as an
intermediate product in the oxidation of phosphorus
to phosphorus pentoxide.   Schenck, Mihr and Banthien[18]
and Scharff[19], who found many points of resemblance
in the properties of slowly oxidising phosphorus and
phosphorus trioxide — for example, the luminescence
of both was inhibited by the same vapours — favoured
Jungfleisch's interpretation of the reaction between
phosphorus and oxygen.

Particularly interesting are the experiments of L. and E. Bloch[20]. They found that if a blast of air was passed over phosphorus in a glass tube the luminosity could be blown off the surface of the phosphorus and maintained at some distance from the solid, a dark interval separating the latter from the luminous cloud. According to the Blochs the phosphorus was oxidised in two stages, first to phosphorus trioxide in the dark interval, and then further to phosphorus pentoxide in the luminous cloud. Weiser and Garrison[21ab] carried out a number of experiments which they believed to be in agreement with this view. When oxygen was passed through a tube containing phosphorus, so that no glow occurred, all of the phosphorus vapour was supposed to be converted into an oxide which oxidised further with luminescence, either on passing the gas into the air or through a tube heated to 65°. This behaviour, which they regarded as characteristic of phosphorus trioxide, was accepted as proof of the formation of phosphorus trioxide in the oxidation of phosphorus. Considering the ease with which the phosphorus trioxide was supposed to be formed it is surprising that Weiser and Garrison did not show its presence analytically or even attempt to collect it by suitable means for identification. Their results /

results are no proof that phosphorus trioxide was responsible for the luminescence.

There is considerable divergency of opinion regarding the properties of phosphorus trioxide itself. For example, Scharff[19] found that for phosphorus trioxide like phosphorus there was a boundary pressure of moist oxygen above which no glowing occurred, but Rinde[22] failed to confirm it. Thorpe and Tutton[16] and Scharff stated that no ozone was formed in the oxidation of phosphorus trioxide, whereas Weiser and Garrison, and Downey[23] claimed that it was.

The conflicting evidence regarding the properties of phosphorus trioxide itself and the unsatisfactory, indirect methods used to demonstrate that phosphorus trioxide was the substance responsible for the chemiluminescence of phosphorus do not warrant an unqualified acceptance of the foregoing theory.

It is significant that Thorpe[24] himself did not attribute the luminosity of phosphorus entirely to phosphorus trioxide, but to the chemical union of oxygen with the vapours of phosphorus and phosphorus trioxide. Lord Rayleigh[25] in a paper dealing with the rate of propagation of the glow of phosphorus definitely stated that he did not find it particularly helpful to assume the two-stage oxidation of phosphorus cited. It is of interest, /

interest, however, that Eméléus[26] found that the
light from slowly oxidising phosphorus trioxide gave
the same ultra-violet band spectrum as the light from
slowly oxidising phosphorus.

If proof of the luminous oxidation of phosphor-
us trioxide during the slow oxidation of phosphorus
is lacking, it is still more surprising to find no
basis for the usual assumption that phosphorus pent-
oxide is the sole final product of the slow oxidation
of phosphorus. I can find no analytical figures to
support the assumption. Russell[9] thought it prob-
able that lower oxides such as P_4O_2 and P_4O_4 (which
gave phosphorus tetroxide on thermal decomposition)
were formed when phosphorus oxidised in moderately
dry oxygen at pressures above 500 mm. Below this
pressure these lower oxides oxidised to phosphorus
pentoxide, but no proof is mentioned.

Jungfleisch[17b] found that the immediate pro-
ducts of the direct and spontaneous oxidation of phos-
phorus in oxygen at low pressure were different from
those obtained at higher pressure. At 18-20 mm.
pressure phosphorus trioxide and a bright yellow com-
pound, supposed to be P_4O, were produced. If the
oxidation was carried out in the presence of water
the aqueous solution contained the products of the
action /

action of water on the oxides formed in the dry gas.
58% of the total phosphorus was converted into phos-
phorous acid.   Jungfleisch stated, however, that in
pure oxygen at atmospheric pressure in the cold phos-
phorus pentoxide was the sole product.   No analytical
results are given.

By the oxidation of phosphorus in oxygen at
very low pressure (0.1-0.5mm.) Kohlschütter and Frum-
kin[27] obtained a red product in which the atomic ratio
of phosphorus to oxygen varied from 1 : 0.1 to 1 : 0.7.
On thermal decomposition the substance gave some crys-
tals of phosphorus tetroxide.

The foregoing papers would lead us to suppose
that phosphorus oxidises spontaneously to phosphorus
pentoxide at moderate pressures of oxygen (say 100 -
800 mm.) but to oxides lower than phosphorus pentoxide
at high or at very low pressures.   This seems unlikely.

Over 100 years ago Thénard[28] analysed the
aqueous acid solution obtained by the slow combustion
of phosphorus in air, in presence of water (Pelletier's
phosphatic acid), and found the atomic ratio of phos-
phorus to combined oxygen to be 1 :2.2.   Dulong[28]
obtained the ratio 1 :2.1 and stated that it was con-
stant and the acid liquid comparatively stable in air.
Later, Salzer[29] found that this liquid contained
hypophosphoric acid, /

acid, phosphorous acid and phosphoric acid, 6-7% of
the total phosphorus being converted into hypophos-
phoric acid.   That is, phosphorus oxidising in oxygen
at a partial pressure of 160 mm. and in presence of
water gives rise to a solution which contains a con-
siderable amount of acids not derived from phosphorus
pentoxide.

Now if Jungfleisch is correct in stating that
phosphorus, water, and oxygen at low pressure give
the same solution of acids, as is obtained by hydrat-
ing the products of the corresponding dry oxidation,
it is difficult to see why this relationship should
cease at higher oxygen pressure.   It seems reasonable
to suppose that Pelletier's phosphatic acid corresponds
in the oxidation of phosphorus in dry oxygen to the
formation of oxides containing at least one constituent
lower than phosphorus pentoxide.

It is apparent then that in the slow combus-
tion of phosphorus we cannot be at all sure either
that phosphorus trioxide, as an intermediate product,
is directly responsible for the observed chemilumin-
escence, or that phosphorus pentoxide is ever the
sole final oxidation product.

In my own research work I have endeavoured to
obtain some idea of the mechanism of the slow oxida-
tion process /

process by studying the properties of phosphorus tri-
oxide itself, and by examining the oxidation products
of phosphorus and phosphorus trioxide.   The results
of my investigations are given in the following pages.

THE PROPERTIES OF PHOSPHORUS TRIOXIDE.

Phosphorus trioxide was prepared according to Thorpe and Tutton's[16] method and obtained as a clear colourless liquid by distillation at low pressure over reduced copper. It solidified to a white wax-like solid which melted at 22.5°. Preliminary tests were made to find its behaviour in oxygen.

At 25° in dry oxygen at various pressures the phosphorus trioxide did not glow but very slowly absorbed oxygen; excessive drying was not necessary to prevent luminescence. When temperature was raised glowing, however, set in and unless care was taken was usually quickly followed by ignition. The temperature of ignition which was quite indefinite, varying from under 50° to well over 70°, did not seem to depend at all on the oxygen pressure. In dry ozonised oxygen steady glowing took place near the surface of the solid oxide.

Many striking effects were obtained in moist air or oxygen. Luminescence, which was in the vapour phase, might be either steady or pulsing, whatever the oxygen pressure, and was seldom observed near the surface of the oxide. Indeed it frequently occurred in narrow connecting tubes attached to the main /

main reaction vessel.   In this the behaviour of phos-
phorus trioxide differed markedly from that of phos-
phorus.   A tendency for a glow to settle on the oxide
was noticed when the latter was moistened by syrupy
liquid derived from phosphorus acids.   No boundary
pressure of moist oxygen was observed above which
glowing ceased.   From the extreme irregularity of the
results it was apparent that at least one very vari-
able factor was present.   It was believed to be mois-
ture.   The three experiments described below illus-
trate the effect of moisture in determining the posi-
tion of glowing.

Experiment 1:-

Air, dried by concentrated sulphuric acid, was passed
at low pressure, 10-12 mm., through a tube on the
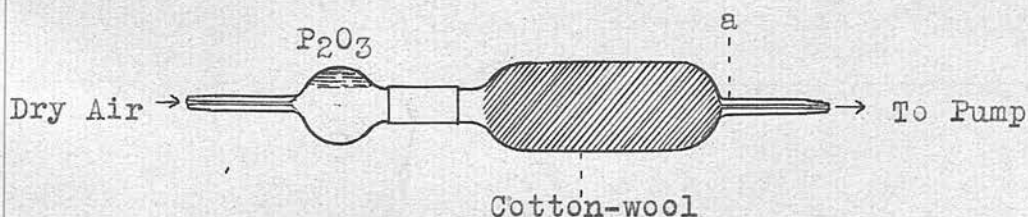upper wall of which was solid phosphorus trioxide.

Fig. 1.

Thence it passed into a wide tube (4cm. diameter)
which was closely packed with undried, or even slightly
damp, cotton-wool.   The /

The latter reached as far as a capillary of 1.5 mm. diameter.   Here at a, immediately beyond the cotton-wool, a small, bright, steady glow established itself, remaining in position for twelve hours and sometimes twenty-four.   Provided that no small crevices were left in the cotton-wool plug, no glowing occurred save at the capillary.   The effect was evidently associated with the water vapour removed by the gas stream from the cotton-wool, as dried cotton-wool was without action.   The test for ozone with potassium iodide-starch paper was readily given in or beyond the glow, but not before it.   When, presumably, all moisture had been removed from the plug, the glow frequently rushed suddenly from the capillary and could not be restored to its original position.

Experiment 2:-

In a closed vertical tube (2cm. diameter) filled with undried oxygen at atmospheric pressure, and containing at the foot a small quantity of phosphorus trioxide, flashing was observed to proceed regularly at the rate of one flash in five minutes, at 15°.   After a flash, which occurred about half an inch above the trioxide, a cloud of minute particles, due to the combustion, was observed to fall, leaving a faint haze behind. The next flash occurred immediately above this haze, the height /

height of which was thereby increased. In one and a half hours the upward advance of the haze was one inch. The occurrence of flashing at ever-increasing distance from the trioxide was attributed to the gradual absorption of moisture by the oxidation product. A similar effect was observed at 8° in oxygen at 1200 mm. pressure.

Experiment 3:-

A slow, steady stream of dry air at 15 mm. pressure was passed over phosphorus trioxide, and then into a long tube, one cm. wide, containing five loosely-fitting rolls of moist filter-paper, ranged four inches apart. A glow was made to settle, with slight adjustment of the air current, in and above the first roll, and remained fairly steady for 50 minutes. The glow then moved along the tube attaching itself to each of the rolls in turn for 5, 10, 20 and again 20 minutes, before finally leaving the tube. The rolls of paper were examined after the experiment and found to be dry. Evidently a glow only settled near a roll of filter-paper when the latter was moist, and moved away when the dry air current and the oxidation product had used up all the moisture. On one occasion a glow traversed fairly quickly, and with much pulsing, a distance of six feet in order to pass to the next moist paper /

paper in a long tube.

The suggestion that water played an essential
part in the luminous oxidation of phosphorus trioxide
was made by Schenck, Mihr and Banthien[18].   Rinde[22]
was of the opinion that in dry oxygen phosphorus tri-
oxide was directly oxidised to phosphorus pentoxide
without glow, but that in moist oxygen an intermediate
compound, possibly phosphine, was formed which oxidised
with glow.   This hypothesis could not be rejected
since phosphorus trioxide was known to react with hot
water with production of spontaneously inflammable
phosphine and might conceivably undergo, to a limited
extent, a similar reaction at ordinary temperature.
Moreover, Labillardière[30] showed that a mixture con-
taining phosphine and oxygen, although it reacted
only very slowly at ordinary pressure, exploded when
pressure was reduced.   Further, Emeléus[26] found
that pure phosphine burning spontaneously in air under
reduced pressure gave an ultra-violet band spectrum
identical with that of glowing phosphorus or phosphor-
us trioxide.

In order to test Rinde's hypothesis evacuated
bulbs containing phosphorus trioxide, and an aqueous
solution of phosphoric acid as source of water vapour,
were set aside at 25° for one or two days.   They were
examined /

examined for pressure change but none was recorded,
thus showing the absence of phosphine.   Rinde's hypoth-
esis did not appear, therefore, to call for further
investigation.

The Rate of Oxidation of Phosphorus Trioxide.

A number of experiments were next performed at
25° to find if the rate of oxidation of phosphorus
trioxide varied in a regular manner with the amount
of water vapour present.   As source of water vapour
the following solutions of orthophosphoric acid were
used:

H_3PO_4 (g. per 100 g. of solution).	Density at 25°.	Aqueous Tension at 25° (mm.)
50	1.335	16.7
80	1.629	4.0
90	1.743	1.2
97	1.845	0.3

The apparatus (Fig. 2) consisted of a bulb into
one end of which was sealed a glass boat.   Phosphorus
trioxide was run into the boat at _a_ and phosphoric
acid into the wide tube at _b_.   On to the apparatus
was sealed a mercury manometer, and the whole was
held pivoted at _c_ so that a rocking movement could be
effected /

effected as shown by the arrow.   The volume of the
bulb was a minimum, 30 c.c., so as to maintain the
saturated-vapour pressure of phosphorus trioxide,
and the rocking device prevented film formation on
the liquids.
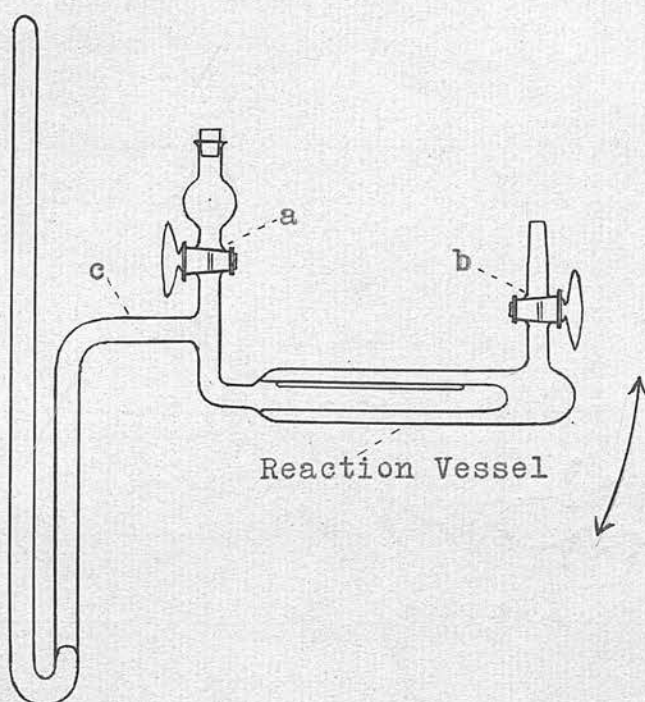
Fig. 2.

In all experiments the same quantities of
liquids were used, viz., 0.2 c.c. of phosphorus tri-
oxide and 8 c.c. of a phosphoric acid solution, a
choice of quantities which did not introduce a marked
change in the pressure of water vapour as the oxide
was used up.   The apparatus containing phosphoric
acid was evacuated /

evacuated, and oxygen, generated by heating potassium permanganate, passed in till its partial pressure was 100-110 mm.   After the apparatus had been heated to 25°, liquid phosphorus trioxide was run into the boat and pressure readings were made at intervals.   The pressure — time curves shown in Fig. 3 illustrate the nature of the results.

Time (minutes).

O Pressure of water vapour 0.3 mm.;
□ 1.2 mm.; × 4.0 mm.; ● 16.7 mm.

Fig. 3.

Experiment 1:-

When the pressure of water vapour was very low — 0.3 mm.—oxygen was absorbed at a slowly increasing rate until all had gone /

gone in one and a half hours.   During oxidation, glow-
ing and flashing took place in the vapour phase, the
luminescence always tending to be away from the phos-
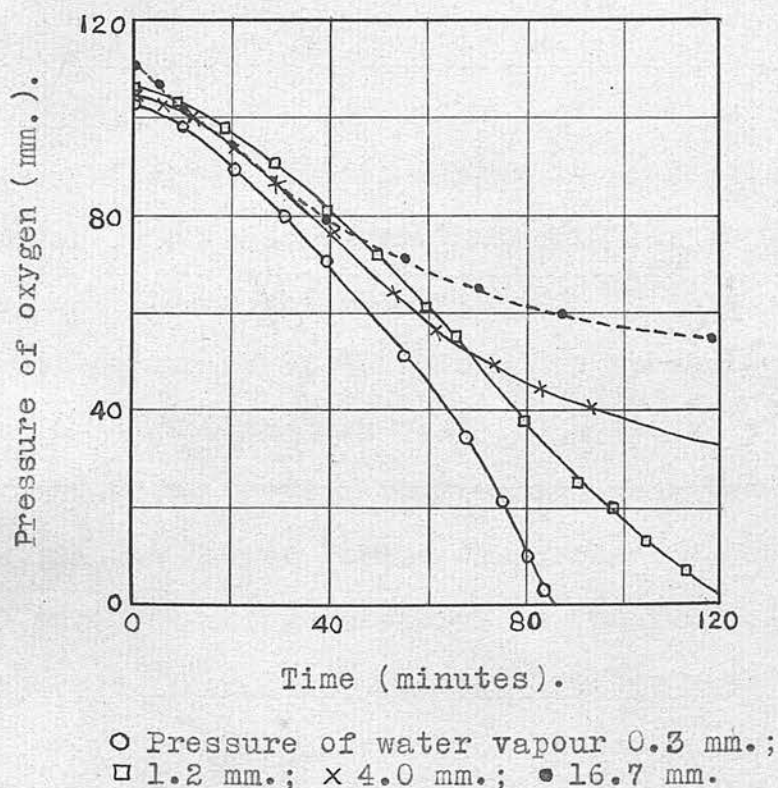phorus trioxide source, i.e., not above the boat.
Luminescence was all the time of the same nature, but
brighter at lower pressures, and it faded and disap-
peared abruptly when nearly all the oxygen was used
up.   Most of the phosphorus trioxide seemed to be
transformed.

Experiment 2:-

The rate of absorption of oxygen in presence of 1.2
mm. pressure of water vapour was similar to that in
experiment 1, but the rate fell off in about 70 minutes.
The glow phenomena up to this point were also similar,
except that glowing took place to a slight extent
above the boat.   After 90 minutes, when the rate of
oxidation was slower, there was permanent glowing
round numerous solid particles in the boat.   This was
not observed when the pressure of water vapour was
very low.   No phosphorus trioxide remained.

Experiment 3:-

When the pressure of water vapour was 4 mm. the rate
of oxidation for 40 minutes was similar to that in the
two preceding experiments.   The glow tended very
early to pass above the boat, and steady glowing show-
ed at numerous points in the boat, earlier than in
experiment 2.   The /

The passing of the glow to the boat coincided with a reduction in the rate of absorption of oxygen and with the disappearance of phosphorus trioxide.

Experiment 4:-

With a high pressure of water vapour, flashing occurred after a few minutes above the boat, and in 10 minutes steady glowing took place in the boat. The phosphorus trioxide was practically all used up. After half an hour the only glowing was that round the solid particles in the boat, and the fairly rapid initial rate of oxygen absorption had given way to a very slow absorption.

In these experiments it was found that the bulk of the phosphorus trioxide was converted into phosphorous acid, which did not absorb oxygen under the conditions prevailing. When the pressure of water vapour was high, this conversion was very rapid, and the subsequent slow rate of oxygen absorption was therefore not due to phosphorus trioxide. In all experiments after the oxygen was used up, a small insoluble residue, consisting of minute particles surrounded by liquid, remained in the boat; this was apparently phosphorus, for it glowed in air. The glowing previously observed in the boat was around these particles. As a test, 40 mg. of phosphorus were disintegrated in 2 c.c. of a 50% solution of phosphoric acid /

acid and part of the mixture was oxidised as in experi-
ments 1—4.   Glowing took place round the solid par-
ticles and the pressure fell at a measurable rate,
depending on the quantity of mixture present and on
the amount of liquid surrounding the particles.   The
appearance of phosphorus in the boat in experiments
1—4 was attributed to phosphorus originally dissolved
in the phosphorus trioxide and set free by the con-
version of the oxide into phosphorous acid.   As the
phosphorus trioxide might contain 1% of phosphorus,
as judged by results of analysis, its rate of oxida-
tion was compared with that of a 1% solution of phos-
phorus in paraffin oil.   With the latter the pressure
of oxygen fell 100 mm. in 3—4 minutes.   This rapid
rate of oxidation therefore bore no resemblance to
the rates found for phosphorus trioxide.   Glowing
appeared only at the surface of the paraffin solution.

The rate of oxygen absorption by phosphorus
trioxide, with low water-vapour pressure, was examined
at constant pressure and volume.   The boat tube was
connected as shown in Fig. 4 with a 45—55 c.c. oxygen
reservoir, to which were attached a mercury manometer,
reading up to 800 mm. pressure, and a flask in which
oxygen was generated by heating potassium permanganate,
and dried by passage through a short column of phos-
phoric oxide.   The/
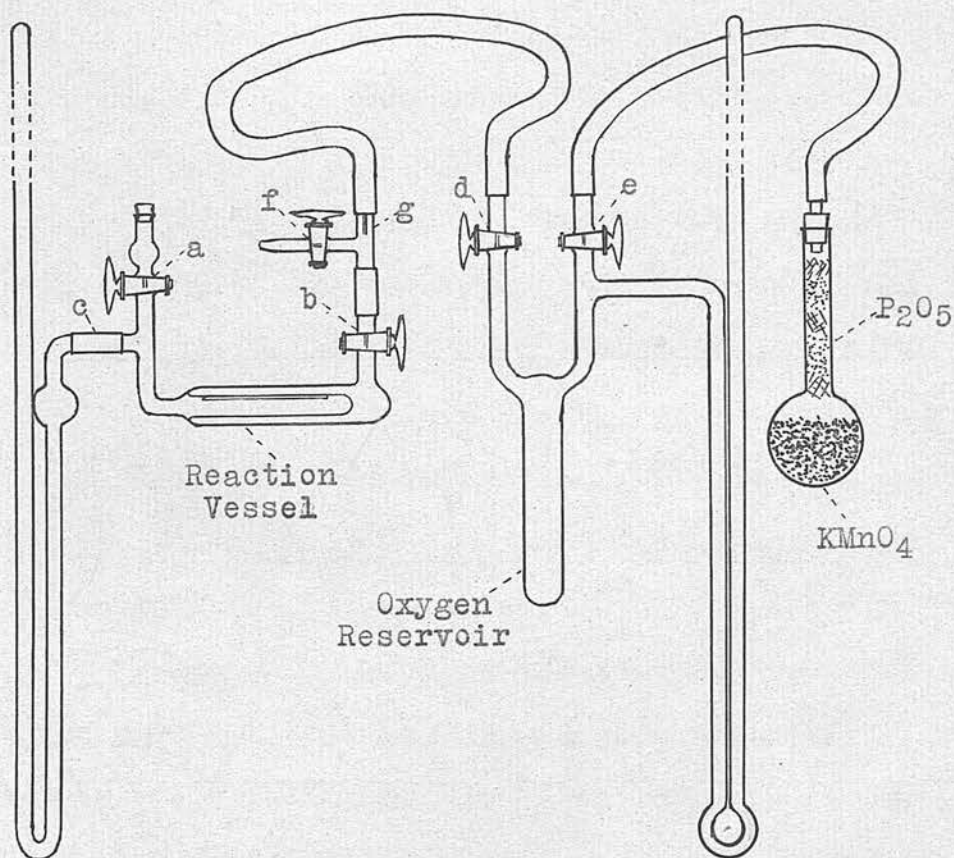
Fig. 4.

The boat apparatus was provided with a manometer,
registering up to 600 mm. pressure, which on account
of its weight was attached at _c_ by means of rubber
tubing to the reaction bulb.   The latter was rocked
up and down as before.   The boat apparatus and as
much as possible of the reservoir were put in a ther-
mostat at 25°.   The volumes of the reaction vessel
and of the reservoir between _b_ and _e_ were known for
all pressures.

In an experiment, the reservoir was charged
with oxygen /

oxygen at a pressure about 300 mm. above the constant
pressure required; 8 c.c. of a 97% solution of phos-
phoric acid and 0.5 g. of phosphorus trioxide were
run into the reaction bulb and the apparatus was
quickly evacuated at f between a and d.   Tap f was
closed and oxygen admitted to the evacuated bulb
through tap b until the pressure was just below that
required.   The rate of inflow was controlled by means
of the narrow capillary, g.   When the apparatus had
been 10 minutes in the thermostat, the pressure in the
reaction vessel was carefully adjusted to the constant-
pressure mark by admitting oxygen from the reservoir.
Immediately after closing tap b, the time was noted
and the pressure in the reservoir read off.   Pressure
in the reaction bulb was next allowed to fall not
more than 5 mm. and then raised by admission of oxy-
gen to about 5 mm. above the constant-pressure mark.
The pressure fell again from this point, and the
times of reaching the constant-pressure mark and the
pressure of the reservoir were noted.   Readings were
made at intervals for one and a half hours or until
the phosphorus trioxide was exhausted.   From the
change in PV, the product of the pressure and the
volume of the reservoir, the amount of oxygen absorbed
in a given time could be determined.   For an experi-
ment performed at 25° /

$25°$ and at constant pressure (100 ± 4 mm.) the results in Table 1 were obtained.

Table 1.

t (mins.).	P (cm.).	V (c.c.).	PV.	$(PV)_0-(PV)_t$ $= (\delta PV)_t$.
0	31.35	50.5	1583	0
7.5	31.0	50.5	1566	17
25	30.15	50.4	1520	63
29.5	29.9	50.4	1507	76
36	29.55	50.35	1487	96
42	29.2	50.3	1469	114
49	28.85	50.3	1451	132
57	28.35	50.25	1425	158
67	27.8	50.2	1395	188
75	27.4	50.15	1374	209
82.5	26.9	50.1	1348	235
90.5	26.4	50.1	1323	260

The change in $\underline{PV}$ in the time $\underline{t}$, $(\delta PV)_t$, was equivalent to the volume of oxygen absorbed (in c.c. at $25°$ and 1 cm. pressure). Except for a slight initial retardation, the rate of absorption was practically constant. Experiments performed with the pressure of oxygen constant at 600, 300, 200, and 50 mm. gave results of the same type, but showing different rates of absorption of oxygen. In order to compare the rates, the amount of oxygen absorbed in 60 minutes, $(\delta PV)_{60}$, was determined for each —

Oxygen pressure (mm.)	600	300	200	100	50
$(\delta PV)_{60}$	119	117	132	169	260

— and the /

the corresponding curve constructed (Fig. 5). It
was unnecessary to correct for the change in volume
of the reaction vessel with pressure, for the reaction
only took place in the bulb part, which was the same
for all.

$$(\delta PV)_{60}.$$
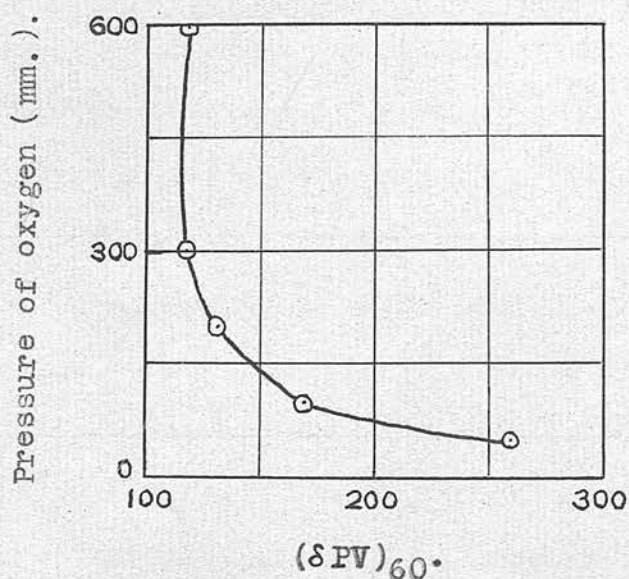
Fig. 5.

An experiment at 25 mm. pressure was unsatis-
factory, as the rate of oxidation on two occasions
suddenly increased considerably. Fig. 5 indicates
that the rate of oxygen absorption may become very
great at pressures below 50 mm., an indication, prob-
ably, of ignition. The results, which were all ob-
tained with one specimen of phosphorus trioxide,
showed that the rate of absorption of oxygen between
600 and 300 mm. pressure /

pressure was practically constant but increased regularly as the pressure fell below 300 mm.   This bore a resemblance to the rate of oxidation of phosphorus in moderately dried oxygen, as found by Russell[9].

In all experiments the position of the luminescence was striking.   Bright flashing occurred principally below the boat, just above the acid surface, or at the end of the tube beyond the boat, i.e., away from the source of phosphorus trioxide and near the water-vapour source.   Attention has already been directed to the appearance of luminescence at sources of moisture at considerable distances from the oxide (pp. 12-14).   Owing to the ease with which phosphorus trioxide took up water-vapour in a partially evacuated apparatus, it was difficult to imagine that in every instance phosphorus trioxide existed where luminescence appeared.   Could the luminescence have been due to dissolved phosphorus?   And if so, why did not luminescence appear at the surface of the liquid oxide as in the case of phosphorus dissolved in paraffin oil?   The only explanation seemed to be that phosphorus trioxide prevented the luminescence of phosphorus.   Phosphorus trioxide vapour containing phosphorus would therefore only luminescence if something were present to destroy the phosphorus trioxide. Water-vapour /

Water-vapour, which is essential for the luminescence at the ordinary temperature, has this effect. One would then expect phosphorus trioxide to destroy the glow of slowly oxidising phosphorus. The following experiments were performed with a 1% solution of phosphorus in paraffin oil.

Experiment 1:-

Over a drop of phosphorus trioxide solidified on a watch glass was put about 0.5 c.c. of the solution, and on another watch glass some of the solution alone. Both solutions glowed brightly. The watch glass with phosphorus trioxide was then placed on the hand in order to melt the oxide. A dark patch developed in the glowing disc and on shaking, to mix in the phosphorus trioxide, darkness gradually spread over the whole disc till the glow was completely quenched.

Experiment 2:-

Below the boat of the apparatus shown in Fig. 2, 5c.c. of the paraffin solution were introduced. Oxygen was present initially at 50 mm. pressure, and the solution glowed quite brightly at the surface. The pressure fell 29 mm. in 28 minutes. The experiment was started afresh, and after a minute 0.5 g. of phosphorus trioxide was run into the boat. The glow was immediately extinguished, and the pressure afterwards fell only 16 mm. in 170 minutes.

Experiment 3:-

Into the boat of a similar apparatus were put 5 c.c.
of the paraffin solution, and below it 8 c.c. of a
97% aqueous solution of phosphoric acid.   When oxygen
was present at 50 mm. pressure the surface of the
paraffin solution glowed brightly.   0.3 g. of phos-
phorus trioxide was run into the boat and the appara-
tus was rocked up and down.   Glowing entirely disap-
peared from the surface of the paraffin but there was
vivid glowing at the end of the tube beyond the boat
(compare p. 26), and a great deal of flashing accord-
ing with the movement of the phosphoric acid.   Brisk
oxidation occurred.   After half an hour the glow was
tending to move back to the paraffin solution, owing
to exhaustion of the phosphorus trioxide.   Admixture
of more trioxide again caused its departure.

These observations favoured the foregoing ex-
planation that the glowing of phosphorus trioxide
might be due to dissolved phosphorus.

THE PREPARATION AND PROPERTIES OF PURE PHOSPHORUS TRIOXIDE.

Owing to its mode of preparation, the crude phosphorus trioxide contained phosphorus, which was no doubt partly removed by distillation.   When the distillation proceeded too far, small globules of phosphorus accompanied the liquid phosphorus trioxide into the receiver and appeared not to dissolve to any extent.   The phosphorus trioxide ordinarily used was therefore probably a saturated solution of phosphorus in phosphorus trioxide.   Distillation over copper was not specially effective in removing phosphorus. Analysis suggested the presence in the oxide of 1% of phosphorus.   The well-known reddening of phosphorus trioxide in light has also been attributed to dis-solved phosphorus.   It is significant that the actual extent of decomposition is slight; for instance, Thorpe and Tutton[31] found only 1% of red phosphorus in a sample of oxide exposed for seven months to light.

In order to determine the part, if any, played by phosphorus in the luminous oxidation of phosphorus trioxide, it was obvious that the preparation of a phosphorus-free oxide was desirable.   An unsuccessful attempt was made to dehydrate pure phosphorous acid. In another attempt /

attempt phosphorus trioxide was exposed to light in
an evacuated bulb, and the oxide was volatilised from
the red solid at 25° into a second bulb where it was
again exposed.   Reddening occurred as before and the
process was once more repeated.   The reddening effect
was purely a superficial one.   The light seemed to
affect the white, opaque phosphorus trioxide, not the
transparent crystals which sometimes formed.   If the
latter were melted and resolidified, they gave a white
opaque solid which was affected by light.   As there
was apparently no diminution in the amount of redden-
ing in the third bulb, this attempt to separate phos-
phorus was temporarily abandoned.   (See, however,
p. 44)

The next method adopted was the recrystallisa-
tion of freshly distilled phosphorus trioxide from a
suitable solvent.   Carbon disulphide is by far the
best solvent for phosphorus but phosphorus trioxide
also dissolves readily.   A preliminary trial showed,
however, that it could be employed if the temperature
of recrystallisation was about -18° and the amount
used was small.   The solvent was dried and distilled
over mercury before use.   Carbon disulphide is known
to be a strong inhibitor of the glow of phosphorus,
but it was found that there was no diminution of the
glowing /

glowing of a specimen of phosphorus trioxide after it had been dissolved in carbon disulphide and the solvent removed by evaporation, finally with the aid of a pump.

The Recrystallisation of Phosphorus Trioxide.

As a trial a small quantity of freshly distilled phosphorus trioxide was recrystallised four times from carbon disulphide in an atmosphere of carbon dioxide. The solvent was then expelled by a fairly rapid stream of carbon dioxide, and the purified oxide, about 25% of the original bulk, transferred to a boat apparatus (Fig. 2) and oxidised at 25° in presence of a 97% solution of phosphoric acid and oxygen at a constant pressure of 100 mm. (compare p. 22). At first no glowing was seen, but after a time there were occasional bright flashes without pressure change in 50 minutes. It was suspected that a trace of carbon disulphide was responsible for the lack of oxidation. The apparatus was therefore re-evacuated and fresh oxygen passed in. Slight glowing occurred and the pressure fall corresponded to $(\delta PV)_{40} = 5.2$. After a further evacuation and addition of oxygen the pressure fall was practically the same. The rate of oxidation /

oxidation of ordinary distilled phosphorus trioxide
was previously found to be represented by $(\delta PV)_{40} =$
108 (see Table 1.), therefore the rate of oxidation
of the purified oxide was reduced to one-twentieth of
the original, probably corresponding to a similar re-
duction in the amount of dissolved phosphorus.   The
phosphorus trioxide obtained from the mother-liquor
was found to oxidise at the normal rate.

    These results showed that greater care had to
be taken in eliminating solvent from the purified
oxide.   The apparatus shown in Fig. 6 was designed
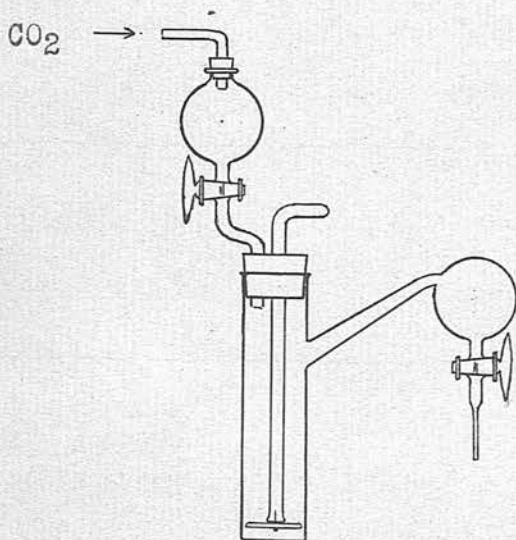for recrystallisation experiments.   It consisted of

$CO_2 \rightarrow$

Fig. 6.

a flat-bottomed tube provided with a side tube through
which the mother-liquor from the crystals could be
poured.   It was /

was further provided with a rubber stopper holding a small tap-funnel, and with a glass rod to which was attached by platinum at the lower end a perforated porcelain disc of nearly the same diameter as the tube. The disc could be moved up and down the tube like a piston. Dry carbon dioxide was passed into the apparatus as shown. Freshly distilled phosphorus trioxide and carbon disulphide were mixed by stirring, in the tube, and cooled to -18°, the perforated disc being moved up and down to prevent formation of crystals on the walls. The crystals were then allowed to settle and the disc was pressed down to force out the liquor. The latter was quickly poured off into the side bulb and thence removed. The recrystallisation was repeated and the crystals were finally washed with cooled carbon disulphide. The purified oxide was melted, transferred to a small tube, and solvent removed by evacuation with an oil pump, the oxide meanwhile being many times melted and resolidified. The yield of oxide was slightly higher than before. The specimen glowed when rubbed on the fingers, and in ozonised oxygen, but did not ignite on cotton wool. When oxidised according to the usual method the amount of oxygen absorbed was $(\delta PV)_{40} = 9$, slightly more than before, and there was quite bright flashing at intervals. On the assumption /

assumption that phosphorus trioxide absorbed no oxygen the maximum amount of oxygen absorbed by this oxide corresponded to little more than 0.1% of dissolved phosphorus.

Light petroleum (b.p. 40—60°) was tried in case the preceding results were due to carbon disulphide. Recrystallisation was effected five times and the solvent removed as before. The amount of oxygen absorbed by a portion of the oxide was equivalent to $(\delta PV)_{40} = 27$, three times the value found above. If the oxidation was due to phosphorus alone, this result indicated that there was three times as much phosphorus left in the oxide as in the preceding experiment and one-quarter of the amount present in the ordinary distilled oxide for which $(\delta PV)_{40}$ was 108. One might expect to obtain identical results for the rate of absorption of oxygen by the three specimens of phosphorus trioxide obtained by saturating the two purified oxides and the unpurified oxide (if not already saturated) with phosphorus at 25°. For the first two the values of $(\delta PV)_{40}$ were found to be 92 and 90, and for the last, 100. The two lower values were attributed to the fact that only minimum quantities of the solutions were prepared and phosphorus separated slightly while the oxides were being measured out. This did not happen with the third specimen. The value /

value 100 was lower than that previously obtained for
phosphorus trioxide, viz., 108.   The latter value was
due to the use of oxide melted at 30—40°, which con-
tained sufficient phosphorus to saturate it at a temp-
erature above 25° and more than enough to saturate it
at 25°.

The recrystallisation of a much larger quantity
of phosphorus trioxide was attempted.   Light petroleum
was apparently not so effective as carbon disulphide
in removing phosphorus, but it had the advantage that
larger quantities could be used.   A combination of
methods was therefore adopted, the recrystallisation
being effected with carbon disulphide and the crystals
washed with light petroleum.   40 c.c. of freshly dis-
tilled phosphorus trioxide were mixed with one-third
of the volume of pure carbon disulphide and recrystal-
lised at -18°.   The crystals were pressed as free as
possible of liquor and washed with 15 c.c. of cooled
light petroleum.   The process was twice repeated with
diminishing quantities of the solvents, and followed
by two final washings with light petroleum (5 c.c. and
10 c.c.).   The crystals were melted and filtered
through glass wool into a bottle from which air was
displaced by dry carbon dioxide.   The yield was about
one-third of the original bulk.

The oxide /

oxide in the mother-liquors was recovered, excess of phosphorus removed, and the oxide distilled and re-crystallised as before.   In all, three products were obtained and put in one bottle from which the remain-ing solvent was carefully removed as before.   The phosphorus trioxide in the last mother-liquor was re-covered from solution in the usual manner and distill-ed in a vacuum to give a clear phosphorus-saturated solution of phosphorus trioxide.

A little of the purified oxide was oxidised in presence of 3 mm. of water vapour.   The total amount of oxygen absorbed, if due to oxidation of phosphorus alone, corresponded to about 0.02% of dissolved phos-phorus.   Bright flashing occurred under the boat during the first half hour; after three hours no glow-ing was seen and the pressure remained steady.   This experiment indicated further removal of phosphorus from the oxide.   A drop of this purified material when rubbed on the fingers gave a bright but momentary glow, whereas a drop of the ordinary oxide gave a glow sufficiently bright and lasting to illuminate the whole hand.   It was supposed that the purified oxide glowed and absorbed a minute quantity of oxygen because of the retention of a trace of phosphorus.   Elimina-tion of this trace by further recrystallisation was impracticable, /

impracticable, but it was thought that it might be
eradicated by exposure of the oxide to sunlight, a
process in which there was no further introduction of
substances with an inhibitory effect on the glow.
According to expectations the oxide reddened in sun-
light, but not to the extent shown by the unpurified
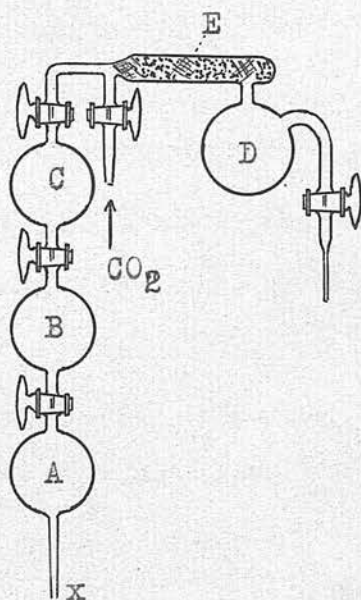oxide.   The apparatus shown in Fig. 7 was designed.

Fig. 7.

Initially only that part was used which consisted of
the three glass bulbs joined together as indicated.
Phosphorus trioxide was drawn into bulb A and x was
sealed off.   The three bulbs were then thoroughly
evacuated and the taps closed.   As large a surface
as possible of the phosphorus trioxide was exposed to
light /

light for a few hours and considerable reddening took place.   The apparatus was re-evacuated and the phosphorus trioxide in bulb A volatilised into bulb B by heating A to 40° and cooling B.. The oxide was again exposed to light, whereupon further reddening occurred, and then transferred to bulb C for a third exposure. In bulbs B and C the reddening was not so extensive as in bulb A.   The second part of the apparatus, which had not been contaminated with phosphorus trioxide vapour containing phosphorus, was now sealed on to the three bulbs, and the tube E charged with phosphoric oxide.   The whole apparatus was evacuated and the phosphorus trioxide in bulb C volatilised through the phosphoric oxide into the receiving bulb D.   The drying tube and the bulb D were then filled with pure, dry carbon dioxide to atmospheric pressure, and portions of the oxide were removed as required.

The Properties of Purified Phosphorus Trioxide.

At the ordinary temperature the oxide was a transparent, crystalline solid, lacking the opaque, waxy appearance of the unpurified product, caused probably by the separation of phosphorus from solution, on solidification.

A clear, colourless sample /

sample of purified phosphorus trioxide contained in
an evacuated bulb was exposed to light for ten weeks
in a well-lit laboratory, but although it was several
times melted and resolidified, it remained colourless
and transparent.   Crude phosphorus trioxide similarly
treated was readily affected by light (see p. 30).
A second sample of purified oxide, which was kept in
an atmosphere of carbon dioxide and used for the fol-
lowing experiments, was also exposed to light.   The
colourless crystalline mass assumed, during the first
few hours' exposure, a faint pink tinge which did not
deepen on further exposure for six weeks.   The colour
was due to the separation of a very small quantity of
red substance.

When rubbed on the fingers the purified oxide
gave no glow, and for a short time there was a pungent
acid smell resembling that of hydrochloric acid.   The
phosphorus smell so readily detected with ordinary
phosphorus trioxide was entirely absent.   The pure
oxide when spread on cloth did not ignite as does the
ordinary product, but when mixed with a small propor-
tion of the crude oxide, or with phosphorus, glowing
and ignition were restored.

The melting points of the purified and unpuri-
fied oxides were determined in a vacuum in small melt-
ing-point tubes, the oxide in each case having been
initially volatilised /

volatilised through phosphoric oxide.   The values
found were:

> Purified oxide . . . . . 23.8°
> Unpurified oxide . . . . 22.4°

In order to obtain an indication of the amount
of phosphorus dissolved in the unpurified oxide, the
depression constant of the pure oxide was found by de-
termining by Rast's[32] method the lowering of freez-
ing point produced by naphthalene as solute.   With
solutions containing 1.98 and 2.67% of naphthalene
the lowerings were 1.85° and 2.4° respectively, giving
for the depression constant the values 11,700 and
11,200.   For the lowering of freezing point produced
by phosphorus, viz., 1.4°, a depression constant of
11,000 gives 1.6 g. as the amount of phosphorus (as
P_4) dissolved in 100 g. of trioxide.

The pure oxide and the oxide saturated with
phosphorus at 25° were analysed quantitatively.
0.15—0.25 g. was melted under water in a small Kjel-
dahl flask and heated at 40—50° till converted into
phosphorous acid.   The pure oxide left no residue,
whereas the unpurified oxide left a residue of phos-
phorus.   An excess of liquid bromine was added and
then 3—4 c.c. of 4N-sodium hydroxide, since hypo-
bromite was found to oxidise phosphorous acid effec-
tively (see p. 64).   Phosphorus was also completely
oxidised.   After /

After a short time 5 c.c. of concentrated nitric acid were added and the solution was boiled to free it from bromine.   The phosphoric acid was precipitated twice as magnesium ammonium phosphate, which was converted into pyrophosphate.   The following results were obtained:

	Wt. of oxide	Wt. of $Mg_2P_2O_7$	% of P_4O_6
Purified oxide	0.1968 g.	0.3984 g.	100.04
	0.1468 g.	0.2972 g.	100.05
Unpurified oxide	0.1579 g.	0.3239 g.	101.37
	0.2530 g.	0.5195 g.	101.47

On the assumption that the purified oxide was entirely free from phosphorus, the two results for the unpurified oxide correspond respectively to 1.74 and 1.87 g. of free phosphorus in 100 g. of the trioxide.

The solubility of phosphorus in the purified oxide at 25° was determined by shaking a weighed excess of purified phosphorus with about 1 g. of phosphorus trioxide in a small stoppered tube, in an atmosphere of carbon dioxide.   The tube was first heated sufficiently to melt the phosphorus and then allowed to stand at 25°.   The excess of phosphorus collected into a globule which was easily removed, washed, and weighed.   The weight of phosphorus dissolved corresponded to 1.71 g. /

1.71 g. per 100 g. of trioxide, the three determina-
tions of the solubility of phosphorus in phosphorus
trioxide therefore showing satisfactory agreement.

The behaviour of the purified oxide in oxygen
was studied. At 25° and in presence of 4 mm. of
water vapour, the oxide neither glowed nor absorbed
oxygen at 100 mm. or 18 mm. pressure, in contradis-
tinction to the absorption of oxygen, accompanied by
luminescence, exhibited by impure phosphorus trioxide
(see experiment 3, p. 19). At higher temperatures,
the following phenomena were noticed. 0.2—0.3 g.
of oxide was mixed with phosphoric oxide and volatil-
ised into a 6 c.c. bulb into which pure dry oxygen
was passed to a pressure of 300 mm. The bulb was
sealed and heated gradually, but no glowing or fuming
was seen below 200°. At about 220°, fuming was ob-
served, accompanied by a very faint glow. The action
was not brisk, for after heating for a quarter of an
hour at this temperature oxygen was still present.
With undried phosphorus trioxide and moist oxygen the
result was much the same, but in a second similar
experiment oxidation appeared at 130°. Unpurified
phosphorus trioxide gave an entirely different result,
igniting at 40° in dry oxygen at 300 mm. pressure and
using up all the oxygen. When ozonised oxygen con-
taining 1% of ozone /

ozone was passed at a slow rate over the pure phos-
phorus trioxide at 25°, oxidation occurred without
luminescence. Under similar conditions, ordinary
phosphorus trioxide glowed brightly and difficulty was
experienced in preventing ignition.

When the purified oxide was melted under excess
of water and heated gradually, it was simply converted
into phosphorous acid, until a temperature of 75—80°
was reached. At this point decomposition set in,
bubbles of gas passed up through the water from the
oxide, and yellow and red solid products were formed.
The gas fumed at the surface of the water, and gave
bright flashes. Unpurified phosphorus trioxide ex-
hibited the same phenomena at a somewhat lower temp-
erature.

When purified phosphorus trioxide in excess
was sealed in an evacuated bulb with a small quantity
of water, a clear yellow syrup formed, which after
several days became opaque. The bulb was opened
under water but no gas was present. The amount of
yellow substance was too small for accurate analysis,
but it contained a greater proportion of phosphorus
than phosphorus trioxide. In its behaviour it re-
sembled the yellow substance prepared by Chalk and
Partington[33] from phosphorus trichloride and phos-
phorous acid below 70°.

When the purified oxide was heated in a vacuum
at 300°, red, yellow, and white decomposition products
were formed, phosphorus tetroxide being amongst them.
The thermal decomposition of ordinary phosphorus tri-
oxide gives a similar result.

A portion of the pure trioxide was saturated
with purified phosphorus at 25°.   The oxide so ob-
tained assumed on solidification the white, opaque
appearance of unpurified phosphorus trioxide, glowed
in air, ignited on cloth, and reddened in light.   It
was therefore concluded that the properties previously
supposed to be characteristic of phosphorus trioxide
were directly attributable to the presence of dis-
solved phosphorus.

The Preparation of Pure Phosphorus Trioxide
without the Aid of Solvents.

It was now obvious that the failure to obtain
pure phosphorus trioxide by the light exposure treat-
ment only (see p. 30) was due to the insufficient
number of exposures.   The procedure was therefore
repeated with only a few grams of oxide.   During
exposure to light the oxide was frequently melted and
resolidified, and when the surface of the bulb was
covered all over /

over with red phosphorus so that light could no longer
penetrate, the oxide was transferred by volatilisation
to another bulb.   Exposure in twelve bulbs was neces-
sary to effect complete removal of phosphorus.   As
anticipated the oxide had exactly the same appearance
as that prepared by recrystallisation, and it also
gave no glow when rubbed on the fingers.   This proved
definitely that the absence of glowing in the oxide
prepared by recrystallisation was not due to inhibi-
tion of the glow by traces of solvents.

THE INHIBITION OF THE GLOW OF PHOSPHORUS.

a) <u>Inhibition by phosphorus trioxide:</u>—

On p. 26 mention was made of a probable inhibitory
effect of phosphorus trioxide on the glow of phosphor-
us.   This is not an unusual phenomenon as Emeléus
has shown that sulphur dioxide inhibits the glow of
sulphur[34] and, possibly, arsenic trioxide the glow of
arsenic[35].   The following experiments further illus-
trate this inhibitory effect in the case of phosphorus
trioxide.

Experiment 1:—

To each of two 8 c.c. bulbs were added a little phos-
phoric oxide and 30 mg. of phosphorus which had been
dried with filter paper.   One bulb contained in ad-
dition a drop of phosphorus trioxide.   Both were
charged with oxygen to atmospheric pressure, sealed,
and heated up slowly in a beaker of water.   In the
bulb that contained no phosphorus trioxide the phos-
phorus glowed at 21° and ignited at 23°, but in the
other, glowing did not appear round the phosphorus
until the temperature reached 51°, and ignition only
took place at 58°.

Experiment 2:—

An apparatus was arranged (Fig. 8) whereby either dry
air alone,/

alone, or dry air charged with phosphorus trioxide
vapour, could be passed over a piece of porous tile
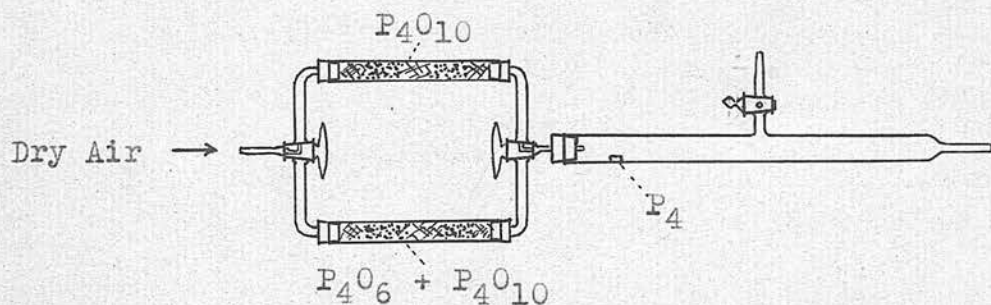impregnated with phosphorus.

Fig. 8.

When air alone at the rate of 15 c.c. a minute
was passed over the tile it glowed distinctly and no
other glow was visible.   If, however, the air was
then directed through the tube containing phosphorus
trioxide the glow on the phosphorus was extinguished
in 5 seconds, and after 90 seconds a luminous cloud
appeared in the atmosphere beyond the end of the tube.
The appearance of this cloud was attributed to the
partial destruction of the inhibiting oxide by atmos-
pheric moisture.   On reversion to the phosphorus
trioxide-free air current the glow on the tile was re-
stored in 30 seconds and a pulse of light travelled
slowly along to the right until it was extinguished
at a distance of 10 cm. from the phosphorus.   The lum-
inous cloud outside the tube disappeared in 100 seconds.

Experiment 3:— /

Experiment 3:—

The side tube shown in Fig. 8 was connected with a
Siemens ozoniser so that ozonised oxygen could be
passed into the long tube.

Air containing phosphorus trioxide vapour was
passed at the rate of 15 c.c. a minute over the phos-
phorus and a glow appeared at the far end of the tube.
When the passage of dry ozonised oxygen (0.5—1% of
ozone) was started at the same rate a glow was immedi-
ately visible at the entry into the wider tube, and
the glow at the end of the tube disappeared in 30
seconds.   Excess of ozone was escaping, which showed
that all the phosphorus trioxide had been destroyed.
When the stream of ozonised oxygen was suspended the
glow in the middle of the long tube moved off slowly
towards the right, becoming fainter, until, finally,
the usual luminescence was established at the end of
the tube.   Similar effects were obtained when the
rates of both gas streams were 3 c.c. a minute.   If
the rate of the air stream was then increased to 36
c.c. a minute no glow was seen where ozone was entering
the wide tube, and excess of phosphorus trioxide was
escaping.

Experiment 4:—

When phosphorus reacts with air in presence of mois-
ture, ozone /

ozone is formed.   It was important to find if a
stream of air passed over moist phosphorus would, in
virtue of the ozone present, restore the glow to air
charged with vapours of phosphorus trioxide and phos-
phorus.   The arrangement was the same as in experi-
ment 3 except that the ozoniser was replaced by a tube
containing phosphorus moistened with water.   Between
this tube and the usual apparatus was a drying bulb
with phosphoric oxide to free the gas from moisture,
which would itself have been capable of restoring the
glow.

The same results were obtained as in experiment
3, except that the effects were not quite so pronoun-
ced owing to the smaller amount of ozone available.
When the moist phosphorus was replaced by dry phos-
phorus no restoration of the glow occurred, which cor-
roborates Russell's[9] statement that no ozone is lib-
erated when dry phosphorus is oxidised.

From these four experiments it is evident that
the glow of phosphorus is inhibited by phosphorus tri-
oxide, and that the inhibitory effect can be removed
by means of moisture or ozone, both of which destroy
phosphorus trioxide.

b) Inhibition by water vapour:—

That phosphorus should cease to glow in moist oxygen above a certain boundary pressure has always been regarded as strange. Russell[9] showed that the effect was associated with water vapour as he failed to obtain a boundary pressure in oxygen dried by concentrated sulphuric acid. Jorissen and Ringer[36] attributed the uncertainty of the values of the boundary pressure to varying amounts of water vapour, thus implying that the boundary pressure was in some way dependent on the moisture content of the oxygen. Later, Lord Rayleigh[37,25] demonstrated that both oxygen and moisture exerted inhibitory effects, the moisture not differing essentially in its mode of action from a typical inhibitor such as camphor.

As no one appears to have studied the effect on the boundary pressure of varying the pressure of water vapour at constant temperature I performed a few rough experiments to test this. Phosphoric acid solutions were used as source of water vapour and oxygen was obtained from a cylinder, but was not examined for nitrogen.

A small piece of purified phosphorus was placed in a tube containing 6 c.c. of a 97% solution of phosphoric acid, and oxygen was added to 1200 mm. pressure. The phosphorus /

phosphorus was shaken up with the acid and allowed to drain, and the tube was immersed in water at 25°. After a few minutes there was a flash above the phosphorus, which lit up and continued to glow steadily, while a pulse of light passed along the tube in each direction and disappeared.   With 90, 80, 70 and 60 % phosphoric acid solutions similar observations were made but with a 50% solution no glow appeared in 20 minutes.   Glowing could be initiated by lowering the pressure or raising the temperature.   Eventually a 52.5% solution, with an aqueous tension of 15.5 mm., was found to correspond to almost complete inhibition of the glow at 1180 mm. pressure of oxygen.   When water (aqueous tension, 24 mm.) replaced phosphoric acid no glowing occurred in oxygen above 980 mm. pressure.

In oxygen at atmospheric pressure and 15° glowing was initiated when the pressure of water vapour was less than 7 mm.

The above results at 25° show that the boundary pressure of oxygen is dependent on the concentration of water vapour.   It is lower, the greater the vapour pressure of water, just as Centnerszwer's[15] results for the inhibitor ethylene show that the partial pressure of oxygen at the glow point is lower, the greater the partial pressure/

pressure of ethylene.   My experiments at 25° and 15°
also indicate that much more water vapour is required
at the higher temperature for complete inhibition
than at the lower, in accordance with Emeléus's[14]
results for ethylene.   It is noteworthy that a con-
siderable amount of water vapour must be present be-
fore glowing in oxygen at high pressure is prevented,
in other words, the oxygen need by no means be dry
for a glow to occur.

The Mutual Interference of Phosphorus Trioxide
and Water Vapour.

Since both phosphorus trioxide and water vapour
inhibit the glow of phosphorus, and the two inhibitors
react with each other, it is obvious that in a system
containing both there must be mutual interference.
When the glow of phosphorus is inhibited by phosphorus
trioxide a small quantity of water vapour should in-
itiate glowing by reducing the concentration of in-
hibiting trioxide molecules.   Conversely, when mois-
ture, in not too great excess, is the inhibiting sub-
stance phosphorus trioxide should restore the glow
by reducing the concentration of water molecules.
Examples of the first case have already been given in
the glowing /

glowing of phosphorus-saturated phosphorus trioxide at 25° in presence of a 97% solution of phosphoric acid (p. 26). In absence of the latter there was no glow (p. 11).

The second case is illustrated by the following experiment — In the boat of the apparatus shown in Fig. 2 was put 0.5 g. of phosphorus-saturated phosphorus trioxide, and below it 6 c.c. of a 50% solution of phosphoric acid. The tube was charged with oxygen at 1200 mm. pressure, kept at 25°, and rocked up and down as usual. A pulse of light passed along the tube every 75 seconds. It was previously found (p. 51) that phosphorus itself did not glow in oxygen at the above pressure in presence of a 50% solution of phosphoric acid. If the acid was replaced by water phosphorus trioxide did not restore a glow. This is to be expected since the vapour pressure of phosphorus trioxide is comparatively low.

The glowing of phosphorus trioxide containing phosphorus in moist oxygen at high pressure, as referred to on p. 14, is also to be attributed to the mutual interference of phosphorus trioxide and water vapour.

It is not difficult to see how doubt arose as to whether or not ozone was formed in the oxidation of phosphorus trioxide /

trioxide containing phosphorus (see p. 6).   When a
mixture containing oxygen and vapours of phosphorus
and phosphorus trioxide reaches a source of water
vapour moisture destroys part of the phosphorus tri-
oxide so that some of the phosphorus is free to react
with oxygen in the presence of moisture (unless the
excess of moisture is too great——p.51).   In this re-
action ozone is produced which usually reacts with
more phosphorus trioxide but under certain circumstan-
ces may not do so, e.g., experiment 1, p. 13.   It is
obvious that ordinarily the oxidation in presence of
moisture of phosphorus trioxide containing phosphorus
will be due to oxidation of both phosphorus and phos-
phorus trioxide.   The results of this aspect of the
subject are given in the section dealing with the ori-
gin of the oxidation products of phosphorus trioxide
containing dissolved phosphorus (pp. 86-103).

The Relative Effects of Different Inhibitors.

          Some idea of the relative effects of the three
inhibitors, phosphorus trioxide, water and ethylene,
was obtained by calculating the ratio of the vapour
pressure of the inhibitor to the vapour pressure of
phosphorus at the point where glowing was initiated.
For ethylene /

ethylene the ratio was derived from Emeléus's[14] graph, representing the effect of concentration of the inhibitor on the temperature at which a glow appeared, in ethylene-air mixtures at constant volume.   An interesting fact came to light, namely, that the partial pressure of ethylene over the temperature range 60— 97° was almost directly proportional to the pressure of phosphorus vapour.   The ratio of the two pressures had the average value, 145.   This direct proportionality is very clearly shown in the following graph.
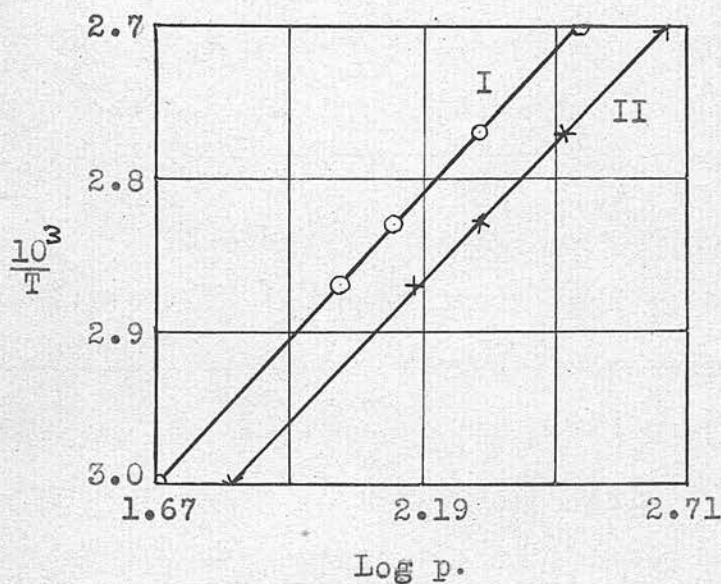

Fig. 9.

Curve I is the usual straight line representing the relation between the logarithm of the vapour pressure of phosphorus and the reciprocal of the absolute temperature ($\times 10^3$).   The vapour pressure /

pressure was multiplied by 100 for ease of comparison.
Curve II which shows the corresponding relation be-
tween the logarithm of the partial pressure of ethyl-
ene at the glow point, and the reciprocal of the ab-
solute temperature ($\times 10^3$) is also a straight line very
nearly parallel to the first.

The oxygen in the mixture apparently exerted
very little effect, showing that if it was itself an
inhibitor its action was weak compared with that of
ethylene.   No doubt its effect would have become
more pronounced at lower temperatures when the ratio
of the oxygen pressure to the vapour pressure of phos-
phorus would have been considerably increased.

The ratio of the vapour pressures of phosphorus
trioxide and phosphorus at the glow point, 51°,(p. 46)
was calculated on the assumption that both phosphorus
trioxide and phosphorus exerted their normal vapour
pressures, viz., 10.3mm.[18] and 0.284 mm.[38] respec-
tively.   The value of the ratio, 37, was probably not
a satisfactory measure of the inhibitory power of the
oxide owing to the preponderance of oxygen (760 mm.).
As it was known, however, that phosphorus-saturated
phosphorus trioxide did not glow in oxygen at low
pressure at 25° where the ratio of the vapour pressures
of phosphorus trioxide and phosphorus was 56, it was
assumed /

assumed that the inhibitory power of phosphorus tri-
oxide could be represented by a number between 40 and
50.

The experiments outlined on p. 51 gave a rough
indication of the inhibitory effect of water.   Water
inhibited the glow of phosphorus at 25° in presence of
oxygen at 980 mm. pressure, the ratio of the vapour
pressures of water and phosphorus being 480.   At low
oxygen pressure this ratio would have had a much high-
er value.

It is evident that phosphorus trioxide is about
three times as powerful an inhibitor as ethylene, and
ethylene probably five times as powerful as water.

THE VAPOUR PRESSURE OF PHOSPHORUS TRIOXIDE.

(A criticism)

The vapour pressure of phosphorus trioxide has been determined by Schenck, Mihr and Banthien[18] over the temperature range 22°—91°.   I have found that if the logarithm of the vapour pressure be plotted against the reciprocal of the absolute temperature the following curve results (Fig. 10).

Log. p.
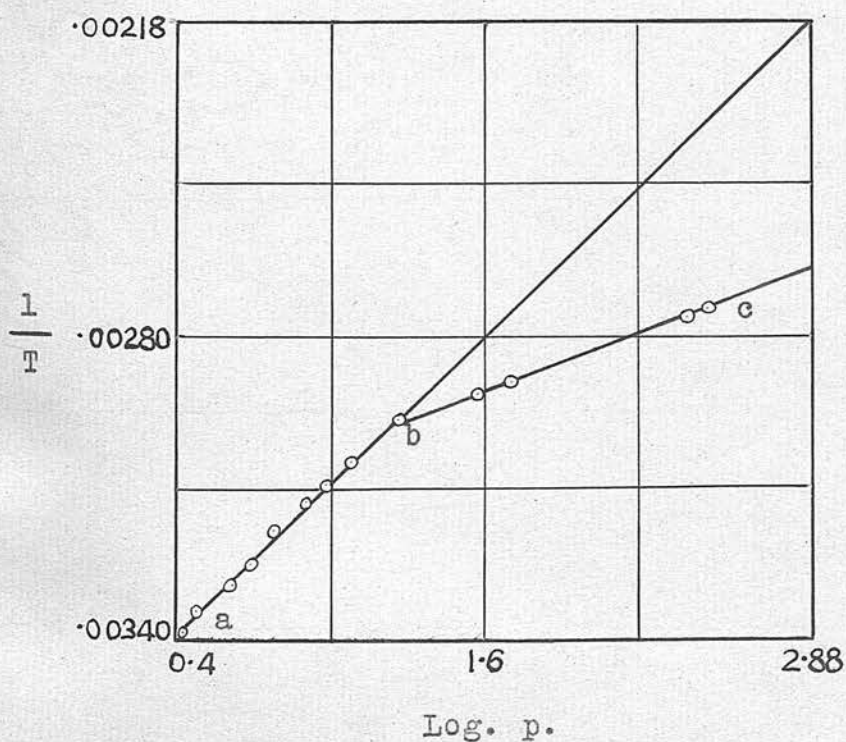
Fig. 10.

The first nine points lie on a straight line ab and the last four on another straight line/which inter-
bc
sects the first /

first where $1/T$ = .00298 (i.e. T = 336°), and if ex-
tended in the other direction meets the line corres-
ponding to log p = 2.881 (p = 760 mm.) where $1/T$ =
.00267.   The boiling point of the liquid is therefore
given by 1/.00267 or 374°abs.   Thorpe and Tutton[16]
found it to be 446°abs.   The boiling point derived
from the graph by extending line ab is 458° ($1/T$ =
.00218).   It follows that Schenck, Mihr and Banthien's
estimations of vapour tension above 65° are wrong,
probably owing to interaction of phosphorus trioxide
and moisture at that temperature with production of
phosphine (see p. 43).

THE OXIDATION PRODUCTS OF PHOSPHORUS AND PHOSPHORUS TRIOXIDE.

In some preliminary experiments undertaken before the preparation of phosphorus-free phosphorus trioxide it was found that phosphorus trioxide (1—2% of phosphorus) oxidising in oxygen at 450 mm. pressure, and in presence of concentrated sulphuric acid as source of water vapour gave a white, solid oxidation product which remained unaltered in bright sunlight and on heating to 100°, but sublimed completely in a vacuum at a temperature below 200°. It was suspected to be phosphorus tetroxide, a substance first prepared by Thorpe and Tutton[39] by the thermal decomposition of phosphorus trioxide.

The sublimate was composed of colourless, transparent, highly lustrous crystals which were submitted to microscopic examination. Although cubical in shape the crystals did not belong to the regular system as they were highly birefringent. Typical crystals are shown in Fig. 11a. The crystallographic features of the oxide were in agreement with Thorpe and Fletcher's[39] observations on phosphorus tetroxide. Since phosphorus pentoxide sublimes quite readily in a vacuum a small amount was sublimed in order to compare its crystals /

crystals with those of the supposed lower oxide.
They were not birefringent and, as shown in Fig. 11b,

(a)   (b)

P_2O_4 P_2O_5
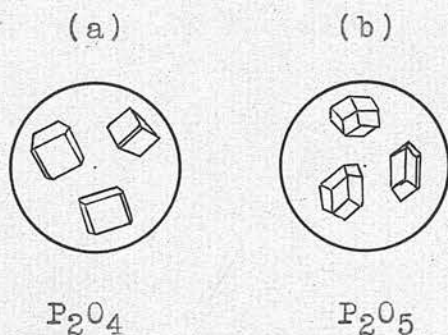
Fig. 11.

were obviously different from those in Fig. 11a.   No
phosphorus pentoxide crystals were observed in the
oxidation product.

Further proof that the oxidation product con-
tained phosphorus tetroxide was obtained.   The sub-
stance was deliquescent, slight fuming occurred when
it was decomposed with water, and the aqueous solution
responded to the tests applied by West[40] to phosphor-
us tetroxide.   The formation of this oxide which was
in all probability phosphorus tetroxide was not due to
the action of phosphorus trioxide on concentrated sul-
phuric acid, since pyrophosphoric acid as source of
water vapour gave the same solid.   It was also found
later that pure phosphorus trioxide gave no deposit in
oxygen in presence of concentrated sulphuric acid.

Since the absorption of oxygen by the phosphorus trioxide containing phosphorus was almost certainly due both to phosphorus and phosphorus trioxide (p. 54) the phosphorus tetroxide was derived either from phosphorus or phosphorus trioxide, or from both.   A piece of phosphorus was next allowed to oxidise at 15° in oxygen at 400 mm. pressure so that a small quantity of oxides could be collected for sublimation in a vacuum.   The oxidation product was sublimed at 200—300° leaving a slight red residue; in the sublimate only the characteristic birefringent crystals of phosphorus tetroxide were visible.

In consequence of these results experiments on the oxidation of phosphorus and phosphorus trioxide were undertaken in order to determine the composition of the oxidation products.   The oxides were collected and weighed, and analysed by the method given below which was suitable for oxides containing phosphorus tetroxide.

Method of Analysis of Oxides containing
Phosphorus Tetroxide.

Owing to the small quantity of oxides usually available considerable care had to be taken during the whole course /

course of analysis.   The reducing power of the oxides
was estimated as well as the total phosphorus.   In
order to ensure complete oxidation it was advisable
to use a strong oxidising agent such as bromine.
According to Thorpe and Tutton[39] phosphorus tetroxide
is decomposed by water into a mixture of phosphorous
and phosphoric acids ——

$$P_2O_4 \xrightarrow{\ +\ H_2O\ } H_3PO_3 + H_3PO_4 \ .$$

The oxidising agent had therefore to be such as would
convert phosphorous acid into phosphoric acid.   Now
Manchot and Steinhäuser[41] showed that bromine in
presence of hydrochloric or sulphuric acid did not
oxidise phosphorous acid completely, but that in pres-
ence of sodium bicarbonate immediate oxidation occurr-
ed.   This suggests that the active oxidising agent is
sodium hypobromite.   After the performance of numer-
ous preliminary experiments a solution of potassium
bromate was utilised as follows for the oxidation.

a) To a solution containing less than 0.05 g. of
phosphorous acid were added 2 c.c. of each of $N.KBrO_3$,
$N.KBr$, $2N.HCl$ solutions.   Ten minutes was allowed
for complete liberation of bromine which was then con-
verted into hypobromite by means of 4 c.c. of $2N.NaOH$
solution.   For immediate and complete oxidation of
the phosphorous acid /

acid it was essential to have the latter present in
the solution before addition of the alkali. As a
precautionary measure an interval of ten minutes was
given for oxidation. Excess of potassium iodide was
added, and then 6 c.c. of 2N.HCl solution to liberate
the bromine which at once reacted with the iodide.
After ten minutes during which time any bromate pro-
duced from the hypobromite would be decomposed again,
the iodine was titrated with a standard 0.02N solution
of sodium thiosulphate. A blank experiment was per-
formed to find the thiosulphate equivalent of the
bromate used.

As a test of the accuracy of the method some
pure phosphorous acid prepared by Grosheintz's[42]
method was analysed. The following results were
obtained:

	(1)	(2)
Wt. of acid taken (g.)	0.0444	0.0257
Wt. found by analysis (g.)	0.0441	0.0260

This method was used for the experiments of
Table 2. As the experimental error was high for very
small amounts of phosphorus tetroxide the method was
subsequently modified, as in b), whereby more accurate
results were obtained.

b) The N.KBr was replaced by a 4N.KBr solution which
helped to retain better the liberated bromine, to the
loss of which, either in the oxidation experiment or
in the blank, the principal experimental error was at-
tributed.   Only five minutes was allowed for libera-
tion of bromine, and then 10 c.c. of a 0.8N.NaOH solu-
tion were added, dilution of the solution being neces-
sary at this stage to ensure complete oxidation.
Thereafter the procedure was the same as in a).   The
following results were obtained with phosphorous acid
and phosphorus-free phosphorus trioxide:

	(1)	(2)	(3)
Wt. of acid taken (g.)	0.0041	0.0107	0.0246
Wt. found by analysis (g.)	0.0041	0.0106	0.0245
Wt. of oxide taken (g.)		0.0611	
Wt. found by analysis (g.)		0.0611	

The following method of estimating the total
phosphate was adopted after the method of estimation
of small quantities of phosphates had been very fully
investigated.

If, after determination of the reducing power,
the amount of phosphorus present in the solution was
thought to be equivalent to less than 0.03 g. of
magnesium pyrophosphate a known amount of a carefully
standardised solution /

solution of sodium phosphate was added.   Slight ex-
cess of concentrated nitric acid (10 c.c.) was intro-
duced and the liquid was boiled to expel iodine and
bromine, and to concentrate.   The liquid was then
made alkaline with ammonia and the phosphate precipi-
tated twice as magnesium ammonium phosphate, according
to the method given in Classen's "Quantitative Analyse",
p. 67.   In order to minimise experimental error a
blank experiment, with a similar amount of phosphate,
was carried out alongside in as nearly as possible
the same way.

The Oxidation Products of Phosphorus in Dry Oxygen.

The method of procedure was to collect in a
weighable form the oxides falling from a glowing phos-
phorus surface and then to analyse quantitatively, by
the foregoing method, the solution obtained by hydrat-
ing the oxides.

Oxidation in pure dry oxygen, at practically
constant pressure, was carried out at about 11° using
the apparatus shown in Fig. 12.   Oxygen was generated
by heating potassium permanganate in a Jena glass
flask and stored over phosphorus pentoxide in the
large (1500 c.c.) bottle, with which was connected
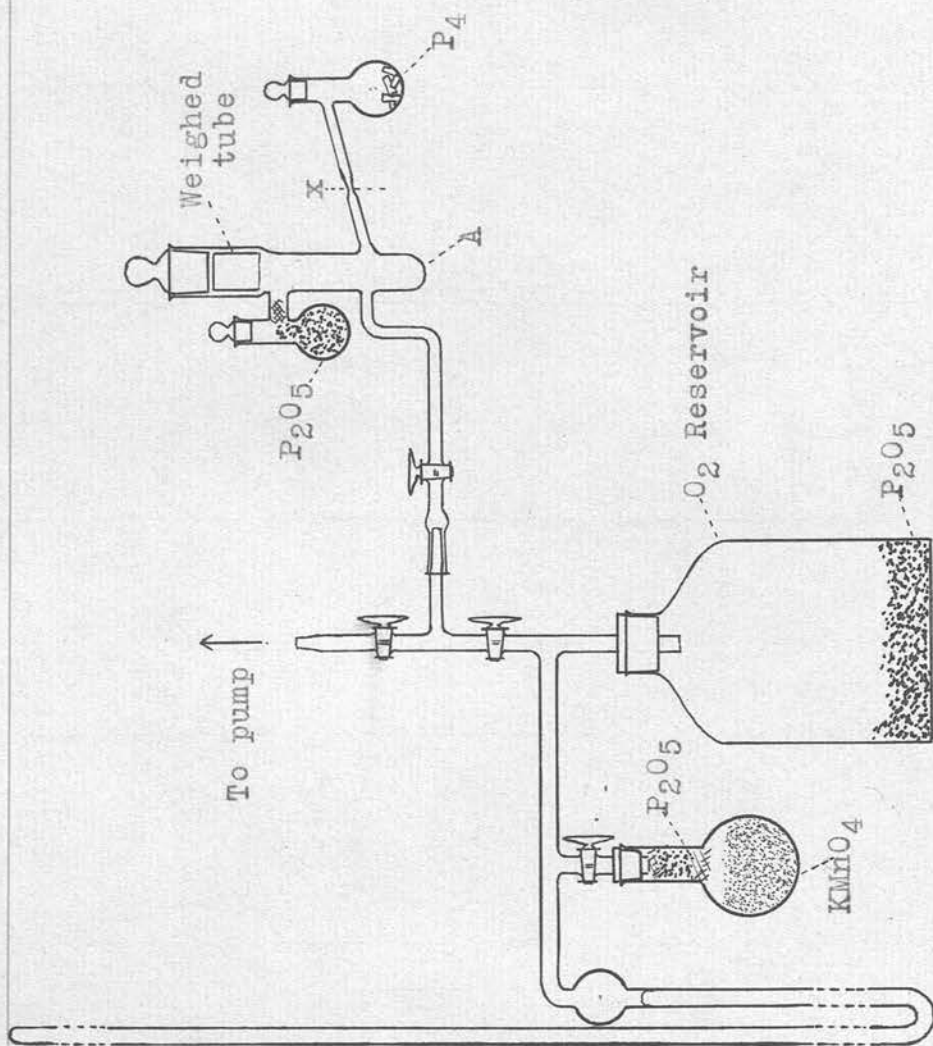a manometer /

Fig. 12.

manometer registering up to 1300 mm. pressure.   The
actual oxidation of phosphorus was performed in the
tube A in which was a small weighed tube, as shown,
for the collection of the oxides.   On to the appara-
tus were sealed a bulb containing phosphoric oxide
and a small distilling flask containing phosphorus
which had been dried in a vacuum over phosphoric oxide.
The apparatus was attached by a ground glass joint
to a tube which could be in communication with an oil
pump or with the oxygen reservoir.

The apparatus was set up as shown, and after
evacuation of tube A left to dry.   Phosphorus was then
distilled into the lower section of A and the distil-
ling flask removed by sealing off at x.   The lower
part of A was cooled in a freezing mixture, and oxygen
from the reservoir was added quickly (to prevent ig-
nition) to any desired pressure over 500 mm.   When
oxidation was to be effected below 500 mm. pressure
oxygen was slowly withdrawn till, after a few minutes,
the required pressure was reached.   This procedure
was necessary to avoid ignition.   It was frequently
found that when oxygen was quickly added to 900—1200
mm. pressure oxidation did not take place.   Oxidation
could, however, be initiated by lowering pressure
until glowing occurred, and then slowly raising it to
the original value.   This effect /

effect was not produced if tube A was dried in vacuo for a short time only, but prolonged drying of the apparatus apparently prevented oxidation in oxygen at high pressure.

In order to collect the oxides tube A was rotated 180° about the ground joint and immersed in water at 11°.   From the continuously glowing phosphorus oxides fell into the weighed tube and, after two or three hours during which the pressure in A had been kept practically constant, the experiment was terminated.   The fact that the glow of the phosphorus was not suppressed showed the absence of an appreciable amount of phosphorus trioxide (see pp. 54 and 56). Tube A was cooled to 0° and the oxygen was replaced by dry air.   The tube with oxides was dropped into a weighing bottle which was immediately weighed, and the oxides, after deliquescence, were analysed in the weighing bottle in the manner indicated.

As expected there was no evidence of volatile phosphorus trioxide in the dry oxides, which were white with a slight yellow tinge (due probably to a trace of amorphous phosphorus) and were apparently unchanged at temperatures up to 100°.   It was noted that the yellow tinge was slightly more pronounced at low oxygen pressure than at high.

The aqueous solution /

solution contained a very small quantity of a yellow
colloidal substance which resembled that prepared from
phosphorus trioxide and water (p. 43).   It was not
taken into account in the analysis since its isolation
was impracticable, and its effect thought to be neg-
ligible.   As the film of oxides on the oxidising
phosphorus had a somewhat yellower tinge than the ox-
ides in the collecting tube no attempt was made to in-
crease the weight of oxides for analysis by removing
from the phosphorus its surface coating of oxides.
At the lowest oxygen pressure tried — 100 mm. — the
film of oxides on the phosphorus surface appeared to
be thicker than at higher pressure, and difficulty
was experienced in collecting sufficient of the fall-
ing oxides for analysis.   Prolongation of an experi-
ment did not markedly increase the yield of oxides,
presumably owing to the film of oxides on the phos-
phorus surface which retarded oxidation.   In any
case the oxides collected after an experiment of con-
siderable duration tended to be yellower in colour,
an undesirable feature in view of the subsequent
neglect of the yellow substance.

If oxidation in tube A was effected with air,
and an oxygen leak from the reservoir instituted to
make good the loss of oxygen, the falling oxides were,
from the first, /

Table 2.

Average temperature of experiment 11°.
Duration of experiment 2-3 hours; *14 hours.

No. of expt.	I Period drying hours	II Press. oxygen mm.	III Wt. of oxides x10⁴ g.	IV Wt. of phosphorus x10⁴ g.	V Wt. of combined oxygen x10⁴ g.	VI Wt. of oxides by analysis x10⁴ g.	VII Atomic ratio P:O	VIII Atomic ratio corrected
1	$\frac{1}{4}$	1240	152	65.1	73.1	138	1:2.17	1:2.13
2*	3	950	117	53.7	61.2	115	1:2.21	1:2.17
3	20	910	165	72.9	81.9	155	1:2.18	1:2.14
4	3	820	136	59.6	67.2	127	1:2.19	1:2.15
5	20	580	104	47.0	53.0	100	1:2.18	1:2.14
6	20	300	129	57.9	65.8	124	1:2.20	1:2.16
7	44	100	65	25.3	29.1	54	1:2.23	1:2.19
8	70	1210	148	69.9	79.4	149	1:2.20	1:2.16
9	400	480	132	61.8	70.4	132	1:2.21	1:2.17
10	20	air	147	67.4	74.0	141	1:2.13	1:2.09

first, yellower than in oxygen, and the film of oxides
adhering to the phosphorus was thinner than usual.

The analytical data relative to the various
experiments are given in Table 2.   The weight of
phosphorus in the oxides (column IV) was calculated
from the weight of magnesium pyrophosphate obtained.
On the assumption that sodium hypobromite completely
oxidised the acids from lower oxides of phosphorus to
acids of phosphorus pentoxide (see however p. 78), the
amount of oxygen combined with the phosphorus was cal-
culated by deducting from the weight of oxygen in the
phosphorus pentoxide corresponding to the total phos-
phorus the amount of oxygen equivalent to the reducing
power of the oxides.   The weight of combined oxygen
is given in column V.   In column VII is given the
atomic ratio of phosphorus to combined oxygen, and in
the last column these values corrected, as mentioned
on p. 78.   Column VI is inserted for comparison with
column III.

Despite the considerable range of pressure the
figures in the last column, for oxidation in oxygen,
are fairly constant, the deviation from the mean —
1:2.16 — not exceeding the experimental error.   The
high value, 1:2.09, for air was probably due to the
greater proportion of the yellow substance.

This ratio of phosphorus to oxygen clearly indicated that neither phosphorus tetroxide nor phosphorus pentoxide alone was the oxidation product of phosphorus, but pointed rather to a mixture of both. As mentioned on p. 69 there was no reason to suppose that phosphorus trioxide came into the question. For the first seven experiments the weight of oxides obtained was greater than that found by analysis (columns III and VI). This was attributed to absorption of moisture by the oxides, the amount being roughly sufficient to convert the calculated proportion of phosphorus pentoxide into phosphoric acid. (Phosphorus tetroxide is not so hygroscopic.) When the apparatus was very thoroughly dried as in experiments 8 and 9 the two weights were the same. It was therefore concluded that phosphorus tetroxide and phosphorus pentoxide, in almost constant proportion, were contained in the oxidation product of phosphorus in pure dry oxygen at pressures between 100mm. and 1200 mm.

In order if possible to confirm this result the oxides were collected in a narrow tube by suitably modifying tube A in Fig. 12. The narrow tube was evacuated and sealed and heated to 300°. As expected the oxides sublimed leaving a small red residue which eventually blackened. /

blackened.   The white sublimate consisted of highly
birefringent crystals of phosphorus tetroxide, and, if
the oxidation apparatus had been initially dried as in
the eighth and ninth experiments of Table 2, of phos-
phorus pentoxide as well.   The result was the same
whether the phosphorus had been oxidised in oxygen at
400 mm. or 1000 mm. pressure.   Oxides shaken from the
phosphorus surface gave the same result.

The Stability of Phosphorus Tetroxide in Oxygen.

As phosphorus tetroxide was evidently a final
product of the slow oxidation of phosphorus it was im-
portant at this point to study the stability of the
oxide in dry oxygen.

Phosphorus tetroxide in as dry a state as poss-
ible was obtained by oxidising phosphorus trioxide
containing phosphorus, in oxygen, in presence of con-
centrated sulphuric acid, and collecting the falling
oxides in a long narrow tube sealed on to the oxida-
tion apparatus (compare Fig. 13).   The narrow tube
was constricted at the middle so that the oxides were
retained in the upper half.   When sufficient had col-
lected the phosphorus trioxide and sulphuric acid were
removed and the oxidation product was sublimed in a
vacuum /

vacuum into the second half of the narrow tube, the
usual small red residue remaining behind.   Oxygen
was added to 160 mm. pressure and the part of the
narrow tube containing the oxide was sealed off.   The
tube was carefully examined under the microscope and
only the characteristic phosphorus tetroxide crystals
were detected.   Under the conditions of the experi-
ment phosphorus pentoxide was not expected to be seen.
It was next heated in a small furnace, and cooled down
at intervals, for examination of the deposited cryst-
als.   Only after heating at 350° was a change noted,
phosphorus pentoxide crystals being found admixed with
those of the tetroxide.   After heating at 410°, how-
ever, practically all were phosphorus pentoxide.
Above 410° the oxides reacted with the glass.   Hence
phosphorus tetroxide oxidises in oxygen at a tempera-
ture of 350°—410°.

Ozonised oxygen, containing 1% of ozone had no
effect on crystals of phosphorus tetroxide at 25°.

The Oxidation of Phosphorus in Air in presence
of Water.

Since the atomic ratio of phosphorus to oxygen
in Table 2 was similar to that found by Thénard[28]
for phosphorus oxidising in air in presence of water
(see p. 8) it was advisable to find if his value could
be repeated.

A slice of phosphorus quarter of an inch thick
was therefore placed in a weighing bottle and water
added to a depth of less than quarter of an inch.
The stopper of the bottle was very loosely inserted
and the whole was set aside at room temperature for
at least a day.   The phosphorus glowed brightly and
ozone was distinctly smelt.   The piece of phosphorus
was then removed and the acid solution filtered and
analysed, the reducing power being determined by the
more accurate method b) given on p. 65.   Hydrogen
peroxide is formed in the oxidation of moist phosphor-
us, but the amount is negligible. (Leeds[43a] obtained
only 1 g. of ozone from the oxidation of over 70 g.
of phosphorus at 18°—21°, and later[43b] he showed
that the amount of hydrogen peroxide produced was
rather less than the amount of ozone.)

The atomic ratio of phosphorus to oxygen for
three experiments was 1:2.25; 1:2.21, 1:2.20.   The
irregularity of the results /

results was traced to incomplete oxidation of the solution by sodium hypobromite.   As phosphorous acid was known to be completely oxidised by this reagent it was supposed that the hypophosphoric acid in the solution (see p. 8) was either not oxidised or only partially oxidised.   Now Salzer[44] has shown that boiling with dilute mineral acids converts hypophosphoric acid into a mixture of phosphorous and phosphoric acids ———

$$2H_2PO_3 \xrightarrow{\;+\;H_2O\;} H_3PO_3 + H_3PO_4$$

In subsequent experiments therefore, the acid solution obtained from oxides of phosphorus was hydrolised by evaporating on the steam bath with a few c.c. of dilute hydrochloric acid, and then oxidised by sodium hypobromite as usual.   Below are given the results of two experiments of two and five days duration respectively:

Table 3.

Wt. of phosphorus from $Mg_2P_2O_7$.	Wt. of combined oxygen.	Atomic ratio P:O
0.0359 g.	0.0406 g.	1:2.19(5)⎫
0.0563 g.	0.0634 g.	1:2.18 ⎬ 1:2.19

The figures in the last column show practically the same atomic ratio of phosphorus to oxygen as was found by Thénard.

Since the oxidation product of phosphorus oxidising in moist air was not completely oxidised by bromine except after hydrolysis it was of importance to re-investigate the oxidation of the aqueous solution derived from the products of oxidation of phosphorus in dry oxygen (pp. 66—74).

Oxidation of phosphorus in dry oxygen at an arbitrary pressure of 900 mm. was carried out and the acid solution was divided into ̮two equal portions.   One was oxidised immediately with sodium hypobromite, the other after heating at 100° with dilute hydrochloric acid.   An increase of 11—12% in the reducing power was observed after hydrolysis.   Consequently the estimated reducing powers of the oxides in all of the experiments of Table 2 were most probably low by about 12%.   A correction of +12% was therefore applied to each, giving the corrected atomic ratios of phosphorus to oxygen shown in the last column of the table (p. 71).

From Tables 2 and 3 it is apparent that, as far as the atomic ratio of phosphorus to oxygen is concerned the oxidation products of phosphorus in dry and moist oxygen are not essentially different.   The higher value of the ratio for the dry oxidation product was probably attributable to the trace of yellow substance, as the acid solution derived from phosphorus, air and water was colourless.

The origin of the formation of hypophosphoric acid in the oxidation of phosphorus has not yet been determined.   It is known that it is not a hydrate of phosphorus tetroxide which gives with water a mixture of phosphorous and phosphoric acids (p. 63).

The Oxidation Products of Phosphorus Trioxide containing Phosphorus.

Since the slow oxidation of phosphorus-saturated phosphorus trioxide is almost certainly due to oxidation of both phosphorus and phosphorus trioxide (p. 54) the oxidation products in oxygen at various pressures were analysed quantitatively in order to find if they differed from those of phosphorus itself. The collection of the small quantity of hygroscopic oxidation product in a dry state was extremely difficult owing to the fact that moisture had to be present in the apparatus for oxidation to occur.

As source of water vapour pyrophosphoric acid was ultimately used.   Its use gave a much smaller yield of oxides than that of concentrated sulphuric acid, which was avoided in case it might introduce complications due to interaction with phosphorus trioxide.   The apparatus shown in Fig. 13 proved to be the most suitable.   The outer vertical tube /

tube was widened at the bottom and into this part
fitted a weighed tube, half an inch long, which was
of the same diameter as the upper portion of the long
tube.   Pyrophosphoric acid was contained in a short
perforated test-tube provided with a wick of glass
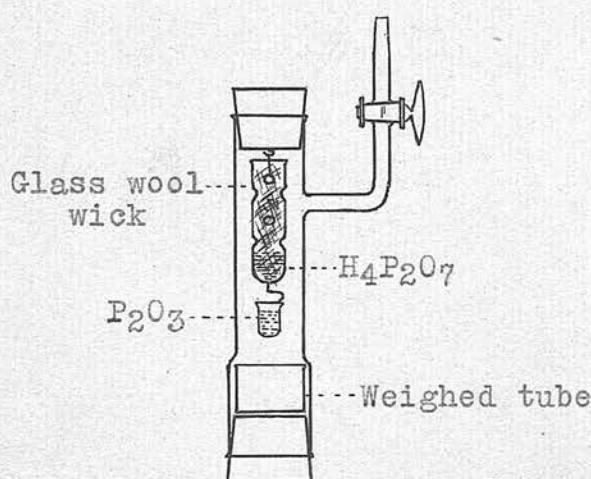wool to increase the acid surface.   A tiny tube with

Glass wool---
wick

$H_4P_2O_7$

P_2O_3

---Weighed tube

Fig. 13.

about 0.2 g. of phosphorus trioxide was sealed on to
the bottom of the acid tube.   Dry oxygen, generated
by heating potassium permanganate, was passed into the
tube to the required pressure.   The experiment was
terminated, usually after a few hours, when a light
snow-like solid had collected in the weighed tube.
Pressure in the apparatus was brought to atmospheric
by the entry of dry air, when necessary.   After the
speedy withdrawal of the trioxide and acid tubes the
apparatus /

Table 4.

Temperature of experiment 25°;   *40°.

No. of expt.	Time of expt. hours.	Press. of oxygen mm.	Wt. of oxides ×10⁴ g.	Wt. of phosphorus ×10⁴ g.	Wt. of combined oxygen ×10⁴ g.	Wt. of oxides by analysis ×10⁴ g.	Atomic ratio P:O
1	19	1150	104	46.8	46.2	93	1:1.91
*2	3	1050	140	63.5	67.6	131	1:2.06
3	4	700	86	40.4	42.7	83	1:2.05
4	5	700	54	23.9	23.3	47	1:1.89
5	6	600	88	40.6	41.9	83	1:2.00

apparatus was thoroughly evacuated to remove trioxide
vapour, and pressure again restored to normal with
dry air.   The lower stopper was carefully removed
and the inner tube was dropped into a weighing bottle
which was immediately closed and weighed.   The oxides
which were pure white were analysed by method b) on
p. 65, and the atomic ratio of phosphorus to combined
oxygen was determined as before.   A representative
set of experiments is given in Table 4 which is drawn
up on similar lines to Table 2.

The figures in the last column suggest at first
glance that phosphorus tetroxide was the oxidation product.
The deviation from the ratio 1:2 required for phos-
phorus tetroxide, in every case, however, exceeds the
experimental error, and the indication in experiments
2 and 3 of the formation of an oxide containing more
than two atoms of oxygen to one of phosphorus is
correct.   The results as a whole may be accounted for
as follows:

When phosphorus in phosphorus trioxide is oxid-
ised in the presence of moisture, which is essential,
phosphorus tetroxide and presumably phosphorus pent-
oxide are formed.   Owing, however, to the presence of
moisture phosphorus pentoxide is almost certainly con-
verted into phosphoric acid; phosphorus tetroxide is
not so readily /

readily hydrated.   At the same time there is a ten-
dency for phosphorus trioxide to react with slight
moisture films on the walls of the apparatus, includ-
ing the weighed tube, so that the oxidation product
is contaminated with phosphorous acid.   The oxidation
product may therefore consist of P_2O_4, P_2O_5 (+ H_2O),
P_2O_3 (+ H_2O).   It is easily seen that the weights of
phosphorus trioxide and phosphorus pentoxide may be
such as to correspond to formation of phosphorus
tetroxide.   This type of result is shown in experi-
ment 5, the atomic ratio of phosphorus to oxygen being
equivalent to formation of phosphorus tetroxide.   The
discrepancy between the fourth and seventh columns
shows, however, that moisture had been absorbed.

    If the amount of phosphorus trioxide is in ex-
cess of the amount of phosphorus pentoxide we have re-
sults such as appear in experiments 1 and 4.   Finally
the oxide may contain phosphorus tetroxide and phos-
phorus pentoxide and still have phosphorus trioxide
partially masking the effect of phosphorus pentoxide.
If phosphorus dissolved in phosphorus trioxide does
in reality give the same oxidation products as phos-
phorus alone, then experiments 2 and 3 are of this type.

    In order to settle this question, if possible,
three more experiments /

Table 5.

Temp. of expt.	Time of expt. hours.	Press. of oxygen mm.	Wt. of oxides ×10⁴ g.	Wt. of phosphorus ×10⁴ g.	Wt. of combined oxygen ×10⁴ g.	Atomic ratio P:O
25°	3	1020	22	10.9	12.4	1:2.20
25°	3	740	28	12.0	13.8	1:2.23
25°	3	400	38	17.3	19.1	1:2.14
50°	2	1000	34	15.5	16.3	1:2.04
50°	2	500	61	30.2	31.7	1:2.03
50°	2	100	49	23.8	23.3	1:1.90
70°	.5	800	89	41.5	41.3	1:1.93
90°	*.12	800	801	357.0	449.0	1:2.44

* ignition.

experiments were made in which the utmost care was
taken to exclude superfluous moisture.   Thus the
weighed tube in the oxidation apparatus was reduced
in size so as to decrease the surface on which phos-
phorus trioxide might give a film of phosphorous acid,
and the apparatus was dried overnight at 100° before
use.   Pyrophosphoric acid was again source of water
vapour and dry oxygen, the pressure of which varied
in the different experiments was passed into the
apparatus as before.   The experiments were performed
at 25° and the duration of each was 3 hours.   The
yields of oxides were very small but they were probab-
ly uncontaminated with phosphorous acid.   The results
are shown in the first three experiments of Table 5.
The mean of the figures in the last column — 1:2.19
— again shows the atomic ratio of phosphorus to oxy-
gen found by Thénard (p. 8) for phosphorus oxidising
in moist oxygen, and indicates that the oxides ob-
tained from phosphorus dissolved in phosphorus triox-
ide are not essentially different from those obtained
from phosphorus alone.

The results of a few experiments performed at
higher temperatures are also given in Table 5.   It is
seen that the values of the ratio in the last column
exceed those at lower temperature, the effect being
specially marked /

marked at low oxygen pressure — 100 mm.   This is to
be expected as phosphorous acid will be more readily
formed at higher temperatures and lower pressures.
A final experiment was performed at a temperature at
which the phosphorus trioxide ignited.   The oxide
analysed was the white product that fell freely from
the burning trioxide, and did not include the red
substance formed, presumably by thermal decomposition,
on the basin containing the trioxide.   Analysis show-
ed that the oxidation product consisted almost entire-
ly of phosphorus pentoxide, the slight reducing power
being due to the small amount of lower oxides formed
during the short pre-ignition period.   (See Table 5.)

The Origin of the Oxidation Products of Phosphorus
Trioxide containing Dissolved Phosphorus.

It has now been found that the oxidation pro-
ducts of phosphorus in presence and absence of water,
and of phosphorus dissolved in phosphorus trioxide,
contain phosphorus and oxygen in much the same atomic
ratio.   As already pointed out (p. 54) oxidation in
the latter case is likely to be due to phosphorus and
phosphorus trioxide, ozone produced by the oxidation
of phosphorus in moist oxygen reacting with phosphorus
trioxide.   The following investigations /

investigations were carried out in order to determine
the nature and extent of this secondary reaction:

a) The oxidation products of phosphorus trioxide in
ozonised oxygen were analysed quantitatively and qual-
itatively.

b) The amount of ozone required for the oxidation of
phosphorus trioxide was found.

c) The total amount of oxygen absorbed by phosphorus
in presence of phosphorus trioxide was found.

a) The oxidation of phosphorus trioxide by ozonised
oxygen:—

Phosphorus-free phosphorus trioxide was oxidised by
oxygen containing about 1% of ozone in the all-glass
apparatus shown in Fig. 14.   The apparatus was at-
tached at X to a drying tube with phosphoric oxide,
which at its other end was connected to a Siemens
ozoniser.   The latter communicated with the oxygen
reservoir shown in Fig. 12.

        The upper part of the apparatus was charged
with phosphoric oxide as shown, and the small weighed
tube was inserted for the collection of oxides.   The
apparatus was left evacuated for at least a day, dry
oxygen was then passed in to atmospheric pressure,
and the small basin containing phosphorus trioxide
was quickly inserted.   Ozonised oxygen /

oxygen containing 1% of ozone was passed through the
apparatus at atmospheric pressure at the rate of 3
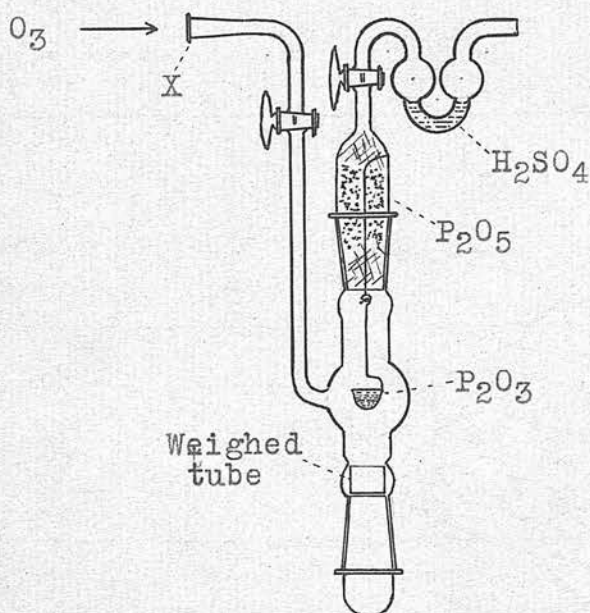c.c. a minute, the oxides falling into the weighed tube.

$O_3 \longrightarrow$

X

H_2SO_4

P_2O_5

P_2O_3

Weighed
tube

Fig. 14.

Experiments were carried out at a temperature of 25°
by immersing the apparatus in a large jar of water
at that temperature.   After 1—1½ hours the passage
of ozone was discontinued, the basin of phosphorus
trioxide was removed, and the apparatus was thorough-
ly evacuated at 30—40° to remove phosphorus trioxide
as vapour.   Dry air was passed into the tube and the
pure white oxides were removed and weighed and anal-
ysed as before.   The aqueous solution of the oxides
contained no yellow substance /

substance (compare p. 70) nor was hydrolysis with hydrochloric acid necessary before oxidation with sodium hypobromite (p. 77). The following results were obtained, the weights of phosphorus and of oxygen in the oxidation products having been estimated as for Tables 2— 5.

Table 6.

Temperature of experiment 25°.

Wt. of phosphorus (g.).	Wt. of combined oxygen (g.).	Atomic ratio P:O
0.0134	0.0151	1:2.18
0.0362	0.0412	1:2.21

The results show that as far as the ratio of phosphorus to oxygen is concerned phosphorus trioxide oxidising in ozonised oxygen gives the same oxidation product as phosphorus oxidising ~~in~~ slowly in oxygen. In order to confirm the results the oxides were collected in a suitable manner for sublimation in a vacuum. The oxides sublimed in the customary fashion giving the clear, cube-shaped, birefringent crystals of phosphorus tetroxide. When special precautions were taken to exclude moisture during oxidation, crystals of phosphorus pentoxide as well as of phosphorus tetroxide were obtained by sublimation.

Consequently when phosphorus trioxide is ox-
idised in ozonised oxygen phosphorus tetroxide and
phosphorus pentoxide are formed, and the atomic ratio
of phosphorus to oxygen (1:2.19(5)) is practically
the same as that found for oxides derived from slowly
oxidising phosphorus.

b) Determination of the amount of ozone taking part
in the oxidation of phosphorus-free phosphorus tri-
oxide.
In the method ultimately adopted two bulbs of equal
capacity were charged with ozonised oxygen of the
same composition, at the same high pressure. The
pressure in each bulb was then slowly reduced until
atmospheric pressure was reached, the gas from one
bulb being passed through a potassium iodide solution
for estimation of the amount of ozone present, and the
gas from the other passed over phosphorus trioxide, the
total weight of deposited oxides from which was found.

The apparatus shown in Fig. 15 was designed
and constructed, and connected by means of a ground
glass joint with a Siemens ozoniser which communi-
cated with the oxygen reservoir shown in Fig. 12.
The volumes of the bulbs A and B between the taps
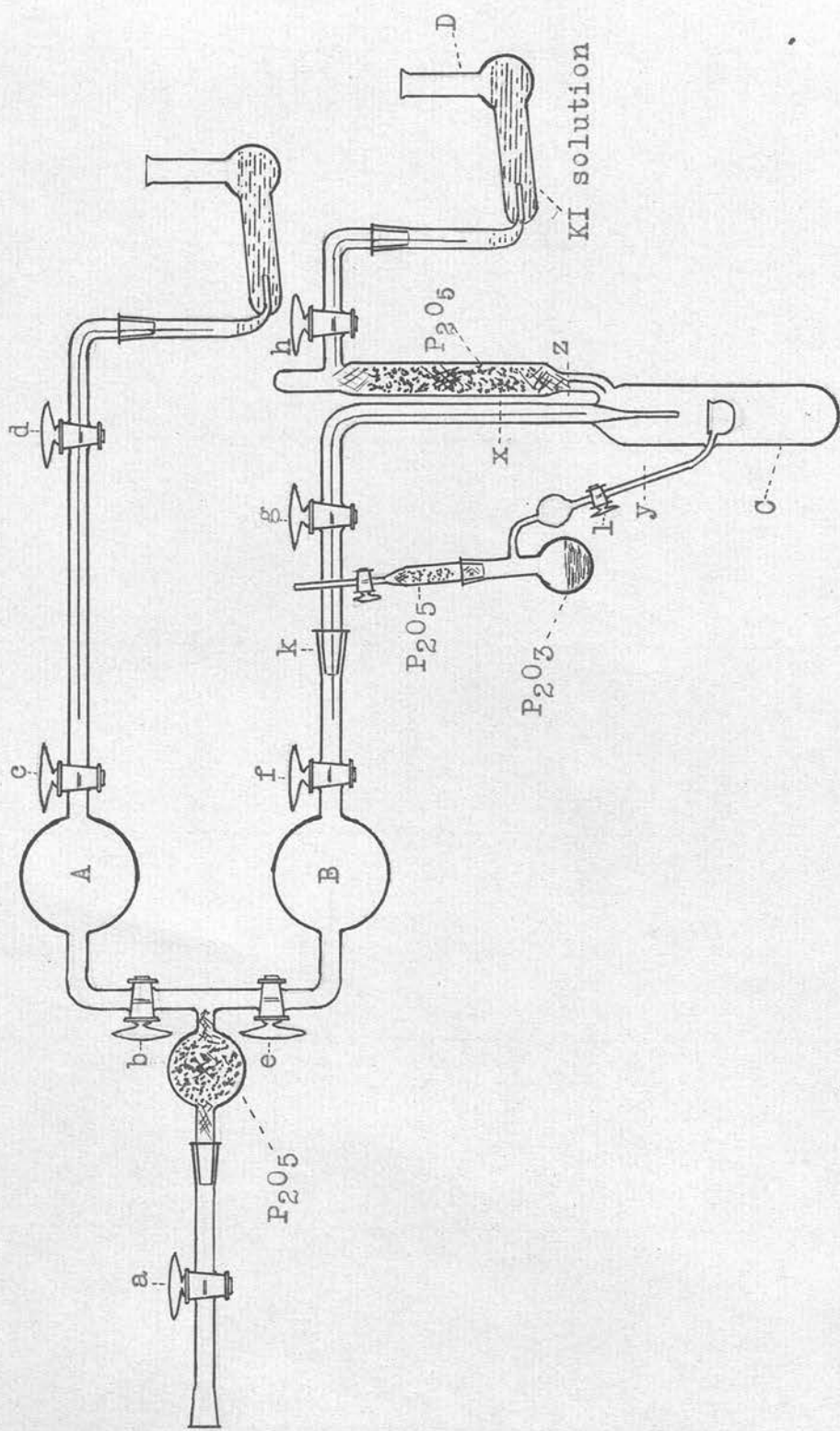were identical (56 c.c.). The tube C in which phos-
phorus trioxide /

Fig. 15.

trioxide was oxidised was made from glass tubing 2 cm. wide and was 10 cm. long.   A small distilling flask for phosphorus trioxide was sealed on to the tube as shown, so that freshly distilled, dry phosphorus tri- oxide could be run into the small cup without intro- ducing moisture.   A narrow drying tube with phos- phoric oxide was sealed on to the top part of the apparatus.   Ozonised oxygen could be introduced just above the surface of the phosphorus trioxide in the cup by means of the entry tube shown.   To the appara- tus were attached two tubes containing potassium iodide solution for absorbing ozone.   The volume of the apparatus between tap c and the point where the ozone reached the absorbing liquid was the same as that between tap f and the point, near the trioxide, where ozone entered tube C.

The whole of the apparatus, except the two absorption bulbs, was fitted together as shown.   The phosphorus trioxide in the small distilling flask was mixed with a little phosphoric oxide and the flask was evacuated.   Into the rest of the apparatus ozonised oxygen was passed and left overnight so as to eliminate traces of substances which might react with ozone.   Afterwards the apparatus was left com- pletely evacuated for 1—3 days.   Dry oxygen was next passed into the apparatus /

apparatus to atmospheric pressure.   The part to the
left of taps c and f was once more evacuated and tap
a closed.   From the reservoir, oxygen at a pressure
of 1300 mm. was slowly passed into the Siemens ozonis-
er in which ozonisation was effected.   When the pres-
sure in the ozoniser was a maximum the reservoir was
shut off and tap a opened so that bulbs A and B were
charged with the same ozonised oxygen to the same
pressure.   The process was repeated until the pres-
sure of gas in the bulbs was about 1300 mm.   Taps
a, b and e were closed.

Phosphorus trioxide was distilled into the
small bulb above tap l and then by means of dry oxy-
gen, at a pressure above atmospheric, forced down into
the cup until that was full.   The two absorption
bulbs were attached and charged with a neutral solu-
tion of potassium iodide, 2% as recommended by Dow-
ney[23].   The tube C was immersed in water at 25°
and ozonised oxygen was slowly passed at the same rate
from each of the bulbs A and B.   The rate of passage
was indicated in the absorption tubes and was care-
fully controlled by means of taps c and d, and f and
g.   The rate was such that all the entering ozone
was used up and that the cloud of oxides formed never
reached as far as the capillary leading to the drying
tube.   This capillary /

capillary served to retain the small quantity of ox-
ides borne by the gas stream.   When the pressure in
bulbs A and B reached atmospheric taps c and f were
closed and b and e simultaneously opened.   By opening
tap a a fresh charge of ozonised oxygen was admitted
to the bulbs and the whole of the above procedure was
repeated.   After 2—4 hours taps c and f were closed
and the apparatus to the left of these evacuated.
Dry oxygen was passed in, and the ozone remaining to
the right of the taps was then forced out.   The ab-
sorption tubes were removed, dilute sulphuric acid was
added to both solutions and the liberated iodine was
titrated with a dilute standard solution of sodium
thiosulphate.   The solution from tube D contained
neither iodine nor phosphate.   The amount of iodine
liberated in the first solution was therefore a meas-
ure of the amount of ozone used in the oxidation of
phosphorus trioxide.

The amount of phosphorus trioxide oxidised was
next determined.   Tube C was disconnected at k and
tilted so that a considerable amount of perfectly
clear phosphorus trioxide could be run back into the
evacuated distilling flask.   If any of the oxidation
product was dissolved in the trioxide the amount was
negligible.   The remainder of the phosphorus trioxide
was removed as vapour /

vapour by prolonged evacuation of the apparatus.
During evacuation the apparatus was sealed off at x
and y in order to eliminate taps g and l at which
leakage might occur, and then heated in water at 50°—
60°.   When removal of phosphorus trioxide was as com-
plete as possible air was slowly passed into the tube,
from which the drying tube was then cut off at z.
The seals at x and y were also broken and the reducing
power of the oxides was ascertained whilst in the ap-
paratus.   A blank experiment was similarly performed,
and then the total weight of phosphorus in the oxides
was estimated as usual.

Although the oxidation product, which was as-
sumed to have the composition $PO_{2.19}$, was contaminated
with a little phosphorus trioxide ($PO_{1.5}$), the above
results were sufficient for the calculation of the
actual weight of phosphorus trioxide oxidised.   The
reducing power of the oxides gave the amount of oxy-
gen required to convert all of the oxides into phos-
phorus pentoxide ($PO_{2.5}$), the total weight of which
was obtained from the amount of magnesium pyrophos-
phate.

If x and y are the number of gram formula
weights of $PO_{2.19}$ and $PO_{1.5}$, respectively, in the
oxides; and if A is the number of gram atoms of oxygen
required /

Table 7.

Vol. 0.01N-thio. equiv. to reducing power (c.c.)	Wt. of Mg$_2$P$_2$O$_7$ (g.).	Vol. 0.01N-thio. equiv. to ozone used (c.c.)	All multiplied by 10^4.				Molec. ratio P$_4$O$_6$:O$_3$
			A	B	C	D	x/4C
95.2	0.1217	23.63	4.76	10.93	1.180	8.94	1.9:1
50.7	0.0571	8.91	2.54	5.13	0.446	3.75	2.1:1

required to oxidise these oxides to $PO_{2.5}$, and B the number of gram formula weights of $PO_{2.5}$ obtained from the oxides after oxidation, then

$$A = .31x + y$$

$$B = x + y$$

i.e. $\quad x = \dfrac{B - A}{.69}$

If C is the number of gram molecules of ozone (O_3) used up in the oxidation (calculated from the volume of sodium thiosulphate solution required to titrate the iodine liberated by the ozone) then the number of molecules of phosphorus trioxide, P_4O_6, reacting with one molecule of ozone is given by x/4C.   The results of two experiments are given in Table 7.

The results show that when phosphorus-free phosphorus trioxide is oxidised by ozonised oxygen two molecules of phosphorus trioxide (P_4O_6) are oxi-dised for every molecule of ozone (O_3) used up. Now in order to convert $2P_4O_6$ into the oxidation pro-duct of composition $PO_{2.19}$, 5.5 atoms of oxygen are required.   Of this a molecule of ozone at most can supply 3, so that oxygen as well as ozone takes part in the oxidation process.

If P_4O_8[*] (see note, next page) and P_4O_{10} are the sole constituents of the oxidation product repres-ented by $PO_{2.19}$, for every molecule of P_4O_8 there must be approximately /

approximately 0.6 molecule of P_4O_{10} present.   The
simplest equation that represents the oxidation pro-
cess is:

$$8P_4O_6 + 4O_3 + 5O_2 = 5P_4O_8^* + 3P_4O_{10},$$
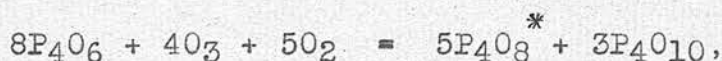
where the amount of ozone used up is equivalent to
the amount of phosphorus pentoxide produced.   The
presence of phosphorus tetroxide in the final oxida-
tion products was not due to incomplete oxidation,
owing to an insufficient supply of ozone, as the tet-
roxide is not attacked by ozone at 25° (p. 75).

The reaction between phosphorus trioxide and
ozone is evidently of a much more complicated nature
than that, for example, between sulphur dioxide and
ozone where one molecule of ozone is entirely used up
in oxidising three molecules of sulphur dioxide to the
trioxide[45], or, between nitrogen peroxide and ozone
where only one of the three oxygen atoms is utilised
in oxidising a molecule of N_2O_4 to N_2O_5.[46]   At pres-
ent it is impossible to say how the ozone molecule be-
haves in the oxidation of phosphorus trioxide, nor
can anything definite /

* P_4O_8 is probably not the correct formula, but it
is used here for simplicity.   From vapour density
determinations West[40] derived the formula P_8O_{16}.

definite be said regarding the different stages of
the reaction.   It has still to be found if varying
the experimental conditions (temperature, oxygen
pressure, etc.) affects the mode of oxidation.

c) Estimation of the total amount of oxygen absorbed
by phosphorus in presence of phosphorus trioxide at
25°:—

In order to find the total amount of oxygen absorbed
by phosphorus in presence of phosphorus trioxide a
known weight of phosphorus in solution in pure phos-
phorus trioxide was oxidised in oxygen in presence
of a small amount of water vapour.   As the phosphorus
trioxide was used up by moisture before the whole of
the phosphorus was oxidised, it was necessary to add,
at intervals, small quantities of phosphorus-free
phosphorus trioxide, until oxidation of phosphorus
was complete.

        The apparatus shown in Fig. 16 was connected
up with an oxygen reservoir provided with a manometer
as indicated on p. 22.   The mercury manometer in
Fig. 16 was shut off from the reaction vessel in case
the mercury would affect the reaction, and for con-
venience the pure phosphorus trioxide was stored in
the bulb included in the manometer section.

2—3 g. of pure phosphorus trioxide were plac-
ed in the bulb shown, and the manometer section was
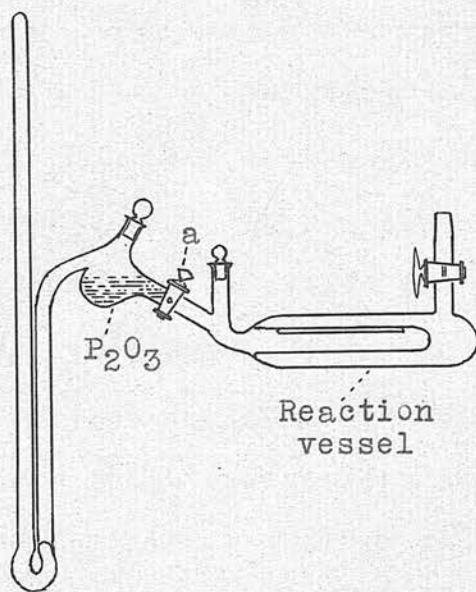evacuated and charged with dry oxygen to a known pres-

Fig. 16.

sure of about 300 mm.   Below the boat in the reaction
vessel were put 8 c.c. of a 97% solution of ortho-
phosphoric acid as source of water vapour.   Air was
then displaced by dry carbon dioxide, and a weighed
amount (0.8—0.9 g.) of phosphorus trioxide saturated
with phosphorus at 25° was introduced into the boat.
The apparatus was attached to the oxygen reservoir
and quickly evacuated.   From the reservoir of oxygen
at a known pressure oxygen was then passed into the
reaction vessel to a pressure of about 300 mm.   The
whole apparatus /

apparatus was kept at 25° and while oxidation proceeded
the reaction vessel was gently rocked to prevent film
formation on the liquids.   As the rate of oxidation
was approximately known (p. 24) the pressure during
oxidation could be kept most of the time within cer-
tain limits by addition of oxygen at intervals from
the reservoir.   When most of the phosphorus trioxide
was used up more was added by momentarily opening tap
a.   After two days when oxidation was practically
complete the reservoir pressure was noted and the
reservoir disconnected.   Tap a was permanently open-
ed and any further slight pressure change noted.
Pressure was constant after another two days.   In a
blank experiment with phosphorous acid replacing
phosphorus and phosphorus trioxide no oxygen was ab-
sorbed in four days.   The volume of every part of the
apparatus was known for all pressures so that it was
easy to calculate the total amount of oxygen used up
in the oxidation.

In Table 8 are the results of two experiments
in which about two-thirds of the total oxygen was
absorbed between 300 and 200 mm. pressure.   As the
apparatus had to be left unattended overnight pressure
unavoidably fell below 200 mm.   The weight of phos-
phorus oxidised was calculated from the weight of
phosphorus-saturated phosphorus trioxide /

Table 8.

| I Wt. of P4O6 g.	II Wt. of P4 g.	III Vol. of O2 absorbed c.c. (N.T.P.)	IV Vol. O2 required by P4	V Vol. O2 available for P4O6	VI Wt. P4O6 oxidised g.	VII Molecular ratio P4O6:P4.
0.813	0.0137	27.28	10.84	16.44	0.1170	4.8:1
0.861	0.0145	30.83	11.47	19.36	0.1378	5.4:1

trioxide used (100 g. of phosphorus trioxide dissolve
1.71 g. of phosphorus at 25°).   In column III is the
total volume of oxygen absorbed, reduced to N.T.P.,
and in column IV the volume required to oxidise the
weight of phosphorus given in column II to the pro-
duct of composition $PO_{2.19}$.   The volume of oxygen
in excess of the latter appears in column V, and in
column VI is the weight of phosphorus trioxide oxidis-
ed to $(PO_{2.19})$ by this volume.   The last column gives
the molecular ratio of the amounts of phosphorus tri-
oxide (P_4O_6) and of phosphorus (P_4) oxidised.

The results show that when phosphorus is oxid-
ised in slightly moist oxygen in presence of an excess
of phosphorus trioxide, the latter as well as phos-
phorus is oxidised.   At 25°, in oxygen at an average
pressure of 200 mm. about five molecules of phosphorus
trioxide (P_4O_6) are oxidised for every molecule of
phosphorus (P_4) undergoing oxidation.   If the oxida-
tion of the trioxide is due to ozone produced in the
oxidation of phosphorus (p. 54), and if two molecules
of phosphorus trioxide are oxidised per ozone molecule,
as at 760 mm. oxygen pressure (p. 97), then the above
five molecules of phosphorus trioxide require for
oxidation two and a half molecules of ozone derived
from the oxidation of one molecule of phosphorus.

Van 't Hoff[47] who studied the oxidation of
phosphorus, at 50°, in air at atmospheric pressure,
and in presence of a dilute solution of indigo as ac-
ceptor, found that for every atom of phosphorus oxid-
ised 0.6 atom of "active" oxygen reacted with the in-
digo (see below).   This is equivalent to the pro-
duction of 2.4 molecules of ozone per reacting phos-
phorus molecule, practically the same result as that
just found under entirely different conditions.

The oxidation of phosphorus trioxide or indigo
during the slow oxidation of phosphorus is an example
of an induced oxidation, a type of secondary reaction
common in autoxidation processes.   A quantitative
study of induced oxidations has revealed that, under
favourable conditions, for every atom of oxygen taken
up by the autoxidisable substance (inductor) an atom
of oxygen ("active" oxygen) is rendered available for
the substance acting as acceptor.   This relationship
is usually explained by supposing that the primary
reaction results in the formation of a peroxide which
then gives up half of its oxygen to the acceptor.

When ozone is formed in the oxidation of phos-
phorus, oxygen itself is supposed to act as acceptor,
the following equations being as a rule adopted to ex-
plain the mechanism[48]:

$$2P + O_2 = P_2O_2; \quad P_2O_2 + O_2 = P_2O + O_3$$
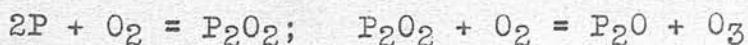
These equations do not represent experimental facts,
however, as both van 't Hoff's result and my own show
that the amount of "active" oxygen or ozone produced
per phosphorus atom oxidised exceeds by 20—25% the
amount indicated in the equations.

I have assumed that ozone formation precedes
the oxidation of phosphorus trioxide, but it may be
that oxidation is effected by "active" oxygen which
in other circumstances would give rise to ozone.   In
order to find if the oxidation of phosphorus trioxide
was induced during the oxidation of phosphorus in dry
oxygen (no ozone is produced) I heated a bulb, con-
taining phosphorus-saturated phosphorus trioxide and
oxygen, at the temperature at which a glow just ap-
peared (oxidation is negligible in absence of glowing).
Unfortunately this condition could not be maintained
long owing to the ready ignition of the phosphorus.
It is therefore not yet possible to say if the oxida-
tion of phosphorus in dry oxygen induces the oxidation
of phosphorus trioxide, or if moisture has a bearing
on the mechanism and extent of the induced oxidation.

THE MECHANISM OF THE REACTION BETWEEN
PHOSPHORUS AND OXYGEN.

As the result of my work the principal support
of the theory that attributes the luminosity of slow-
ly oxidising phosphorus to the oxidation of phosphor-
us trioxide is removed by my proof that phosphorus
trioxide neither glows nor oxidises in oxygen at ord-
inary temperatures.   It is extremely likely, however,
that phosphorus trioxide is formed as an intermediate
compound in the oxidation of phosphorus, since the
final oxidation products of phosphorus in dry oxygen
consist, as I have shown, mainly of phosphorus tetrox-
ide and phosphorus pentoxide, and the same oxidation
products, in similar molecular ratio, are given by
phosphorus trioxide under suitable conditions.

Now I have indicated that phosphorus trioxide
exerts an inhibitory effect on the glow of phosphorus,
from which it follows that if the intermediate com-
pound accumulates in the system during oxidation glow-
ing should cease.   This, however, was not observed
(p. 69), so that the trioxide if formed must undergo
immediate further oxidation.   But phosphorus trioxide
does not oxidise in oxygen at ordinary temperature
unless ozone is present.   In the oxidation of phos-
phorus, therefore, /

therefore, either phosphorus trioxide is oxidised by
active oxygen (or ozone) simultaneously formed in the
reaction, or newly formed molecules of phosphorus
trioxide are sufficiently activated to undergo further
oxidation.   The latter course seems to be the more
likely considering that immediate oxidation of the
trioxide occurs.

Since the oxidation of phosphorus is accom-
panied by chemiluminescence, a phenomenon of frequent
occurrence in autoxidation processes, it is evident
that certain atoms or molecules in the system are
sufficiently excited by the energy liberated in the
reaction to emit light.

The spectrum of glowing phosphorus was examin-
ed by Centnerszwer and Petrikaln[49] and by Emeléus
and Downey[50] who found that it was continuous in the
visible region, but gave a number of bands in the
ultra-violet.   The fact that a band spectrum was
obtained showed its molecular origin.

In the simplest case of chemiluminescence the
heat of reaction remains associated with the reaction
products which are thereby in an activated state, and
may spontaneously revert to the normal inactive state
by emission of light.   It is now known, however, that
the reaction products may transfer their energy with-
out radiation /

radiation to neighbouring molecules, which may then lose their surplus energy by emitting light[51].

In the oxidation of phosphorus the final products of oxidation are phosphorus tetroxide and phosphorus pentoxide. As Ebert and Hoffmann[52] found that purified phosphorus pentoxide showed phosphorescence after exposure to ultra-violet light Kautsky and Zocher[53] suggested that the radiation emitted by oxidising phosphorus was due to phosphorus pentoxide. Eméleus and Purcell[54] found, however, that the spectrum of the phosphorescent glow showed no bands in the ultra-violet, and Petrikaln[55] further indicated that there was no trace of the band spectrum of glowing phosphorus in phosphorus pentoxide excited at 380°. The ultra-violet band spectrum of phosphorus is evidently not attributable to phosphorus pentoxide, but Petrikaln thinks it probable that the continuous spectrum in the visible portion is due to the phosphorescence of phosphorus pentoxide. Nothing can be said as yet regarding phosphorus tetroxide.

Petrikaln next investigated the spectrum due to phosphorus trioxide excited under various conditions, and found that it was the same as that of slowly oxidising phosphorus. It was concluded that the spectrum of glowing phosphorus was due to phosphorus trioxide. Investigation of the absorption spectrum /

spectrum of the oxide gave a result that supported
this conclusion.   Petrikaln supposed that the energy
of formation of phosphorus pentoxide was transferred
by radiation or collision to molecules of phosphorus
trioxide which became excited and emitted the observed
radiation.   This is doubtful, however, as the oxida-
tion products of phosphorus do not contain a surplus
of phosphorus trioxide (p. 69).   If phosphorus tri-
oxide is responsible for light emission, it is more
likely because a small number of the excited trioxide
molecules produced at an intermediate stage in the
oxidation reaction (p. 107), instead of oxidising
further, return to the inactive state with emission of
light.   But the number must be small since phosphorus
trioxide does not accumulate noticeably in the system.
Although the number of molecules responsible for emis-
sion of ultra-violet radiation is unknown it is prob-
ably very small as Bowen and Pells[56] calculated that
only one in 2000 reacting phosphorus molecules was re-
sponsible for the emission of visible radiation.

The validity of Petrikaln's result is, however,
dubitable as his oxide, which was prepared by Biltz
and Gross's[57] method, contained phosphorus..   Until
his experiments are repeated with pure phosphorus tri-
oxide the possibility exists that phosphorus itself is
responsible /

responsible for the characteristic emission.   Petri-
kaln actually found two band systems in the spectrum
of the trioxide, both of which were shown by phosphor-
us compounds in the carbon arc, where reduction to
elementary phosphorus was possible.   An examination
of the absorption and emission spectra of pure phos-
phorus trioxide is contemplated and is expected to
lead to important results.

Dhar[58] has associated the chemiluminescence
of phosphorus, and the formation of ozone, with the
presence of excited phosphorus and oxygen molecules,
produced by absorption of ions liberated during the
oxidation.   But the extent of ionisation is so small
that it is probably not an important source of ex-
cited molecules.   The appearance of ions is an in-
dication of a high energy of reaction.

In any attempt made to explain the mechanism
of the oxidation of phosphorus, account must be taken
of the ease with which the reaction is retarded by
moisture and other stronger poisons.   Russell's[9]
and Scharff's[19] explanations that inhibiting substan-
ces caused formation of protective films on the sur-
face of the phosphorus were shown to be untenable by
Centnerszwer[59], who demonstrated that phosphorus ex-
erted its normal vapour pressure although glowing was
prevented.   Both Gilchrist[60] and Emeléus[14] /

Eméléus[14] have thrown doubt on Schönbein's[61] and Chappuis's[62] explanation that all inhibitors destroyed ozone which was known to promote the glow.   It is now believed that inhibition is due to the failure of the process that propagates the glow, just as carbon tetrachloride added in sufficient quantity to a methane-air mixture prevents the propagation of an explosion wave when the mixture is sparked[63].   Lord Rayleigh[25] and Eméléus[14] have shown that this explanation is probably correct.

According to Lord Rayleigh[37,25] the starting point in the propagation of a luminous wave through a mixture of air and phosphorus vapour is a spontaneous ignition which from a molecular point of view is a rare accident concerning a few molecules only. Propagation of the wave is due to the fact that the products of combustion in one layer of gas facilitate the reaction in the adjacent layer.   Inhibitors spoil this catalytic effect by uniting with or condensing upon the molecules of the reaction products, and rendering them unavailable for inducing the oxidation of neighbouring phosphorus molecules.

That the products of combustion of a reaction as highly exothermic as that between phosphorus and oxygen should have a catalytic effect is not surprising.   In most chemical reactions /

reactions molecules do not react unless they are
"activated" by having imparted to them a certain crit-
ical amount of energy[64]. The molecules of reaction
product in an exothermic process therefore possess,
immediately after their formation, both the heat of
activation and the chemical heat of reaction. These
molecules which are in an energy-rich condition may
communicate their energy to untransformed molecules,
thereby activating them and establishing what are
known as reaction chains (see Christiansen and Kram-
ers[65]). Christiansen pointed out[66] that small
quantities of foreign molecules might inhibit such
reactions, either by taking up the energy from the
"hot" molecules of the reaction products, or by react-
ing with them in some manner, and thereby breaking
the chains. The reaction between phosphorus and
oxygen was cited as possessing the characteristics
of a chain reaction in a high degree.

Bäckström[67], who obtained satisfactory evid-
ence of a chain mechanism in a number of autoxidation
processes extended his investigations to the oxida-
tion of phosphorus. A solution of phosphorus in
heptane or carbon tetrachloride was found to absorb
light of the wave length of that emitted in the lumin-
ous oxidation and the excited molecules so produced
were chemically active. It followed /

followed that part of the radiation emitted in the
slow oxidation was absorbed by phosphorus molecules,
making them chemically active, and that a chain re-
action mechanism was established.   Bäckström was
also of the opinion that the formation of ozone im-
plied the prior production of excited oxygen molecules.
Busse[11] failed to confirm Downey's[23] and Weiser and
Garrison's[21a] result that the ozone was of photo-
chemical origin.

Semenoff[6] obtained further proof of a chain
mechanism in the oxidation of phosphorus.   In his
careful study of the oxidation at low pressures he
found that below a certain pressure oxidation was
negligible but that above it an explosion occurred.

Now Christiansen and Kramers[65] called atten-
tion to the fact that chains may be of two kinds.
In the first set each act of chemical transformation
produces not more than one molecule capable of con-
tinuing the chain; a stationary state is established
 when the number of chains starting in unit time
equals the number terminated.   In the second kind
more than one active molecule is produced at each link
of the chain, and the velocity may increase indefinite-
ly, no stationary state being possible.

Although an active centre is capable of induc-
ing a reaction /

reaction whereby more than one new active centre of the same kind is produced, some active centres may be destroyed by contact with the walls of the vessel, and by deactivating collisions in which no new active centres are formed.   The average number, α, of new active centres, available for the propagation of chains and produced as a result of the reaction of one active centre, may, therefore, be either $<$ or $>$ 1 depending on the size of the vessel and the partial pressure of the components, etc.[68].

According to Semenoff[6] the oxidation of phosphorus is a chain reaction of this type, oxygen atoms being the active centres.   The explanation of the critical pressure is that α is a function of pressure such that $\alpha < 1$ and oxidation is negligible, below the critical pressure, but $\alpha > 1$ and the reaction explosive, above the critical pressure.   In his most recent publication Semenoff[69] has represented the chain mechanism as follows:

1) $O_2 = O + O$ 3) $P_4O + O_2 = P_4O_2 + O$

2) $O + P_4 = P_4O$ 4) $O + P_4 = P_4O$.
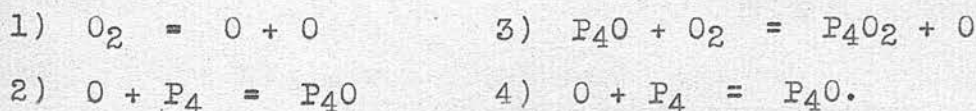
This goes on until the oxygen atom is adsorbed by the wall of the reaction vessel.   Meanwhile P_4O_2 is gradually oxidised in side chains to P_4O_{10}, excited intermediate compounds /

compounds of the type $P_4O_{2n}^*$ being formed, each of
which possesses sufficient energy to dissociate an
oxygen molecule into its atoms. α may therefore ex-
ceed 1.

Since phosphorus and oxygen do not react unless
a trace of moisture is present, and only a very small
number of reaction centres is necessary for combus-
tion to begin when α is >1, it has been suggested
by Semenoff[70] and, independently by Hinshelwood[71],
that the trace of moisture is responsible for the
appearance of a small number of active centres (pro-
duced in some exothermic process), the reaction after-
wards developing of itself.

Semenoff's explanation of the mechanism of oxi-
dation enabled him to represent his results satisfac-
torily, but it is apparent from Bäckström's experi-
ments (p. 112) that excited phosphorus molecules also
take part in the reaction. The formation of amor-
phous phosphorus during the oxidation of phosphorus
(p. 69) is probably due to the interaction of normal
and excited phosphorus molecules. It was noted that
more amorphous phosphorus was formed at low than at
high oxygen pressure, as one would expect, since the
tendency of excited phosphorus molecules to collide
with normal phosphorus molecules would be greater at
low oxygen pressure.

The explanation /

explanation of the mechanism of inhibition is simpler
if excited oxygen molecules or atoms are available.
According to Dhar[72] and Moureu and Dufraisse[73]
oxidisability is a feature of the inhibitors of aut-
oxidation processes.   As a great many of the inhibi-
tors of the oxidation of phosphorus are oxidised by
ozone it is probable that some at least undergo oxi-
dation in breaking the chains, presumably by reacting
with active oxygen.   This induced oxidation must be
ineffective or less effective than the normal reaction
in propagating the chains.   So far, the fate of in-
hibitor molecules in the oxidation of phosphorus is
unknown.   My experiments on the oxidation of phos-
phorus in presence of the inhibitor phosphorus triox-
ide (p. 99) do not give the required information as
they were complicated by the presence of moisture.

The mechanism of inhibition by an excess of
moist oxygen is still obscure.   Nothing is known,
for example, regarding the nature of the slow non-
luminous oxidation, beyond the fact that it takes place
in the vapour phase[4].   As hydrogen peroxide and
ozone are produced in presence of moisture, during
the luminous oxidation, and both are the result of an
endothermic process, Bäckström[67c] inclines to the
opinion that their formation is responsible for the
breaking of chains /

chains and the consequent retardation of oxidation
in moist oxygen.   Ozone, however, reacts with phos-
phorus when the reaction with oxygen is inhibited.
It would therefore be advisable to find the nature
and extent of the reaction that takes place between
phosphorus and ozone when glowing in moist oxygen
is inhibited.

Although the chain reaction theory does not as
yet give a detailed picture of the reaction mechanism
it enables us to see at least a connection between
the many unusual features of the reaction.

Attempts to obtain an insight into the mechan-
ism of the reaction by studying the rate of oxidation
have met with little success.   Ewan[8] thought that
oxygen atoms might take part in the process, but
velocity constants were obtained, from the formula
supposed to represent the rate of reaction, only over
a pressure range of 70 mm.   In a series of careful
experiments with dried and moist phosphorus Russell[9]
failed to represent the velocity of oxidation of dried
phosphorus by a simple expression, and, in consequence,
was unable to introduce a factor for the retarding
effect of moisture.   Zawidzki[74] has recently made
a mathematical analysis of Russell's figures, but al-
though equations have been derived to suit the experi-
mental facts, /

facts, no attempt has been made to interpret them.

It is not surprising that the velocity of oxidation cannot be represented by a simple formula when it is realised how many complications arise in the oxidation of phosphorus to phosphorus tetroxide and phosphorus pentoxide. First of all the reaction must take place in a considerable number of stages, regarding the earlier of which we have no definite information. Of the oxides that may be formed, phosphorus trioxide is an inhibitor of the oxidation, and neither phosphorus trioxide nor phosphorus tetroxide oxidises spontaneously in oxygen. The final oxidation products are both dehydrating agents and must have an effect on the reaction when the inhibitor, water vapour, is a component of the system. Induced oxidations introduce further complications, as ozone, for example, promotes oxidation.

At present it is impossible to submit a scheme in which all of these facts receive full consideration. But no doubt careful study of the numerous characteristic features will eventually provide clues which will lead to a complete elucidation of the reaction mechanism.

SUMMARY.

In order to obtain some idea of the mechanism
of the slow oxidation of phosphorus an examination
was first of all made of the properties of phosphorus
trioxide, which was alleged to be responsible for the
chemiluminescence exhibited by the element.   This
investigation was followed by qualitative and quanti-
tative analyses of the oxidation products of phosphor-
us and phosphorus trioxide.

A study of the rate of absorption of oxygen by
phosphorus trioxide in presence of water vapour at
various pressures led to the conclusion that the lum-
inescence of the oxide was essentially connected with
the presence of dissolved phosphorus.

Phosphorus trioxide, as prepared by Thorpe and
Tutton's method[16], invariably contained phosphorus,
the bulk of which could be removed by several low-
temperature recrystallisations from carbon disulphide.
The remainder was removable by exposure of the oxide
to light and subsequent volatilisation from the red
product.   Elimination of the whole of the phosphorus
by exposure to light, although possible, was a tedi-
ous process.

The purified oxide melted at 23.8°, i.e., 1.4°
higher /

higher than the unpurified product, and lacked many
of the properties formerly attributed to phosphorus
trioxide.   For instance, it neither glowed nor oxid-
ised in moist or dry oxygen at the ordinary tempera-
ture and was unaffected by sunlight.   When it was
heated in a sealed bulb with dry oxygen at 300 mm.
pressure, fuming and very faint glowing were observed
at about 200°.

The trioxide dissolved 1.7 g. of phosphorus
per 100 g. when saturated at 25°, and the solution
showed all the properties previously regarded as
characteristic of phosphorus trioxide.

The glow of phosphorus was inhibited by phos-
phorus trioxide, but the inhibitory effect could be
removed by water vapour or ozone, both of which de-
stroyed the oxide.   It was calculated that the oxide
was three times as powerful an inhibitor as ethylene,
and about fifteen times as powerful as water vapour.

A qualitative test of the oxidation products
of phosphorus in dry oxygen revealed that phosphorus
tetroxide was a constituent.   As phosphorus oxidising
in moist air at ordinary temperature gave a product
of the composition represented by $PO_{2.19}$, the oxida-
tion products of phosphorus in dry oxygen were analys-
ed quantitatively.   At all the pressures of oxygen
tried /

tried (100—1200 mm.), and at a temperature of 11°,
the oxidation product was of practically the same
composition, the atomic ratio of phosphorus to oxygen
being 1:2.16.   It contained phosphorus tetroxide
(about 60%) and phosphorus pentoxide, a trace of amor-
phous phosphorus, and possibly a small quantity of a
substance responsible for the appearance of hypophos-
phoric acid in the aqueous solution.   Phosphorus tri-
oxide was not detected.

Phosphorus tetroxide was stable in oxygen at
ordinary temperature, but underwent oxidation to phos-
phorus pentoxide when heated at 350°—400°.   It was
unattacked by ozone at 25°.

Phosphorus-saturated phosphorus trioxide which
absorbed oxygen at 25°, in presence of a small quan-
tity of water vapour, gave an oxidation product of the
composition represented by $PO_{2.19}$.   Phosphorus triox-
ide itself was believed to take part in the oxidation,
as ozone was probably liberated in the oxidation of
the phosphorus, and the trioxide was known to be ox-
idised by ozone.

When pure phosphorus trioxide was oxidised at
25°, by ozonised oxygen, the oxidation product had again
the composition represented by $PO_{2.19}$, and phosphorus
tetroxide and phosphorus pentoxide were the sole con-
stituents.   One molecule of ozone /

ozone was required for the oxidation of two molecules
of phosphorus trioxide (P_4O_6) so that oxygen as well
as ozone took part in the reaction.   By means of
these results it was found that when phosphorus was
oxidised in presence of phosphorus trioxide, and a
small amount of water vapour, five molecules of phos-
phorus trioxide were oxidised for every molecule of
phosphorus undergoing oxidation.

In a discussion of the mechanism of the re-
action between phosphorus and oxygen it was indicated
that phosphorus trioxide is most probably formed at
an intermediate stage in the oxidation of phosphorus.
But it does not accumulate in the system, and probably
undergoes oxidation while in an activated state.
Active molecules of phosphorus trioxide may be re-
sponsible for the chemiluminescence exhibited by slow-
ly oxidising phosphorus, but this point has still to
be settled.

LIST OF REFERENCES.

1) Brandt   Handbook of Chemistry—Gmelin, 1849, $\underline{2}$, 102.

2) Davy,   A Comprehensive Treatise on Inorganic
   Berthollet   and Theoretical Chemistry—Mellor, 1928, $\underline{8}$, 773.

3) Joubert   Ann. École. Norm., 1874, (2), $\underline{3}$, 209.

4) Rayleigh   Proc. Roy. Soc., 1926, $\underline{A\ 106}$, 1.

5) Chariton   Z. Physik, 1926, $\underline{39}$, 547.
   and Walta

6) Semenoff   Z. Physik, 1927, $\underline{46}$, 109.

7) Baker   Phil. Trans., 1888, $\underline{A\ 179}$, 571.

8) Ewan   Phil. Mag., 1897, (5), $\underline{38}$, 505.

9) Russell   J. Chem. Soc., 1903, $\underline{83}$, 1263.

10) Schönbein   Pogg. Ann., 1845, $\underline{65}$, 69, 161.

11) Busse   Ann. Physik, 1927, IV, $\underline{82}$, 873; IV, $\underline{83}$, 80.

12) Harms   J. Chem. Soc. Abs.-, 1904, $\underline{86(2)}$, 331.

13) Graham   Pogg. Ann., 1829, $\underline{17}$, 375.

14) Emeléus   J. Chem. Soc., 1926, 1336.

15) Centnerszwer Z. phys. Chem., 1898, $\underline{26}$, 1.

16) Thorpe and   J. Chem. Soc., 1890, $\underline{57}$, 569.
    Tutton

17) Jungfleisch   a) Comptes rendus, 1905, $\underline{140}$, 444.
                  b) Comptes rendus, 1907, $\underline{145}$, 325.

18) Schenck, Mihr Ber., 1906, $\underline{39(2)}$, 1506.
    and Banthien

19) Scharff   Z. phys. Chem., 1908, $\underline{62}$, 179.

20) L. and E. Bloch   Comptes rendus, 1908, $\underline{147}$, 842.

21) Weiser and Garrison   a) J. Phys. Chem., 1921, 25, 349.
b) J. Phys. Chem., 1921, 25, 473.

22) Rinde   Arkiv. Kemi. Min. Geol., 1917, 7, no.7.

23) Downey   J. Chem. Soc., 1924, 125, 347.

24) Thorpe   Chem. News, 1890, 61, 140.

25) Rayleigh   Proc. Roy. Soc., 1923, A 104, 322.

26) Emeléus   J. Chem. Soc., 1925, 127, 1362.

27) Kohlschütter and Frumkin   Ber., 1914, 47(1), 1088.

28) Thénard, Dulong   Handbook of Chemistry—Gmelin, 1849, 2, 121.

29) Salzer   Lieb. Ann., 1878, 194, 28.

30) Labillardière   Handbook of Chemistry—Gmelin, 1849, 2, 141.

31) Thorpe and Tutton   J. Chem. Soc., 1891, 59, 1019.

32) Rast   Ber., 1922, 55, 1051.

33) Chalk and Partington   J. Chem. Soc., 1927, 1930.

34) Emeléus   J. Chem. Soc., 1928, 1942.

35) Emeléus   J. Chem. Soc., 1927, 783.

36) Jorissen and Ringer   Chem. News, 1905, 92, 150.

37) Rayleigh   Proc. Roy. Soc., 1921, A 99, 372.

38) MacRae and van Voorhis   J. Amer. Chem. Soc., 1921, 43, 547.

39) Thorpe and Tutton   J. Chem. Soc., 1886, 49, 833.

40) West   J. Chem. Soc., 1902, 81, 923.

41) Manchot and Steinhäuser   Z. anorg. Chem., 1924, 138, 304.

42.) Grosheintz   Bull. Soc. Chim., 1877, 27, 433.

43) Leeds   a) Chem. News, 1879, 40, 70.
b) Chem. News, 1881, 43, 97.

44) Salzer   Lieb. Ann., 1877, 187, 322.

45) Abegg   Anorganische Chemie, 1927, 4,1,1, 393.

46) Mellor   A Comprehensive Treatise on Inorganic and Theoretical Chemistry, 1928, 8, 539.

47) Van 't Hoff   Z. phys. Chem., 1895, 16, 411.

48) Abegg   Anorganische Chemie, 1927, 4,1,1, 68.

49) Centnerszwer and Petrikaln   Z. phys. Chem., 1912, 80, 235.

50) Emeléus and Downey   J. Chem. Soc., 1924, 125, 2491.

51) Kautsky   Trans. Farad. Soc., 1926, 21, 591.

52) Ebert and Hoffmann   Z. phys. Chem., 1900, 34, 80.

53) Kautsky and Zocher   Z. Elektrochem., 1923, 29, 308.

54) Emeléus and Purcell   J. Chem. Soc., 1927, 788.

55) Petrikaln   Naturwissensch., 1928, 16, 205.
Z. Physik, 1928, 51, 395.

56) Bowen & Pells   J. Chem. Soc., 1927, 1096.

57) Biltz & Gross   Ber., 1919, 52, 762.

58) Dhar   Z. anorg. Chem., 1926, 155, 303.

59) Centnerszwer   Z. phys. Chem., 1913, 85, 99.

60) Gilchrist   Proc. Roy. Soc. Edin., 1923, 43, 197.

61) Schönbein   J. prakt. Chem., 1845, 36, 379.

62) Chappuis   Bull. Soc. Chim., 1881, 35, 418.

63) Jorissen and Velišek   Rec. Trav. Chim., 1924, 43, 80.

64) Hinshelwood   Kinetics of Chemical Change in Gaseous Systems, 1926, 38.

65) Christiansen and Kramers   Z. phys. Chem., 1923, 104, 451.

66) Christiansen   J. Phys. Chem., 1924, 28, 145.
Trans. Farad. Soc., 1928, 24, 596.

67) Bäckström   a) J. Amer. Chem. Soc., 1927, 49, 1460.
b) Meddel. Nobelinst., 1927, 6, No.15.
c) Meddel. Nobelinst., 1927, 6, No.16.

68) Semenoff   Z. Physik, 1928, 48, 571.

69) Semenoff   Z. phys. Chem., 1929, (B) 2, 161.

70) Semenoff   Z. phys. Chem., 1928, (B) 1, 192.

71) Hinshelwood   Trans. Farad. Soc., 1928, 24, 552.

72) Dhar   Z. anorg. Chem., 1925, 144, 289.

73) Moureu and Dufraisse   Chemical Reviews, 1926, 3, No.2, 113.

74) Zawidzki   Z. phys. Chem., 1927, 130, 109.

THE PREPARATION AND PROPERTIES
OF PURE PHOSPHORUS TRIOXIDE.

BY

CHRISTINA CRUICKSHANK MILLER.

CCXL.—*The Preparation and Properties of Pure Phosphorus Trioxide.*

By Christina Cruickshank Miller.

THE luminescence exhibited by slowly oxidising phosphorus trioxide has been frequently commented on and studied since the preparation of the oxide by Thorpe and Tutton (J., 1890, **57**, 545) and their study of its properties. Many have been the attempts to find the relation between the glowing of phosphorus and the glowing of its oxide. Although the best conditions for production of the glow in the two cases are by no means the same, there are several striking

points of resemblance; for example, Emeléus (J., 1925, **127**, 1362) established the identity of the ultra-violet band spectra, and Downey (*ibid.*, 1924, **125**, 347) showed that the light from each is capable of ionising oxygen; also Scharff (*Z. physikal. Chem.*, 1908, **62**, 179) found that substances which inhibit the glow of phosphorus likewise inhibit that of the trioxide.

The possibility of the glow being due to phosphorus in the oxide was considered by Thorpe and Tutton but rejected as unlikely. It is now shown, however, that Thorpe and Tutton did not study an oxide free from phosphorus, and that many properties supposed to be characteristic of phosphorus trioxide may, indeed, be due to dissolved phosphorus.

In an earlier paper (Miller, *Proc. Roy. Soc. Edin.*, 1926, **46**, 76) it was shown that there was a connexion between the glowing of phosphorus trioxide and the presence of water vapour. The effect on phosphorus trioxide, in evacuated bulbs, of water vapour derived from certain salt–hydrate mixtures was such as to indicate the possibility of formation of hydrides of phosphorus. It has since been found, however, that the use of hydrated chlorides and sulphates leads to erroneous results owing to the liberation of hydrogen chloride from chlorides and of sulphur dioxide from sulphates. When chlorides are used, gaseous hydrogen phosphide has been definitely proved to be amongst the final products, but its formation is due to complicated reactions which ensue between the hydrochloric acid and the phosphorus trioxide, not to direct action of aqueous vapour on the trioxide. When sulphates are used no hydrogen phosphide is produced. The very slight increase of pressure observed when water itself was the source of moisture is now attributed to carbon dioxide initially dissolved in the oxide and liberated in part by the conversion of phosphorus trioxide into phosphorous acid. In subsequent experiments water vapour at various pressures was obtained by the use of aqueous solutions of orthophosphoric acid, which produced no pressure change in presence of phosphorus trioxide in evacuated bulbs.

## *The Rate of Oxidation of Phosphorus Trioxide.*

The rate of oxidation in oxygen, at 25°, of phosphorus trioxide, prepared according to Thorpe and Tutton's method and distilled at low pressure over reduced copper gauze, was studied in presence of the following solutions of phosphoric acid :

H_3PO_4 (g. per 100 g. of solution) ...	50	80	90	97
Density at 25°	1·335	1·629	1·743	1·845
Aqueous tension at 25° (mm.)	16·7	4·0	1·2	0·2

(If moisture was excluded from the apparatus oxygen was absorbed at an extremely slow rate.)

The apparatus (shown to the left in Fig. 1) was a slight modification of that used with hydrate mixtures (*loc. cit.*) and consisted of a bulb into one end of which was sealed a glass boat. Phosphorus trioxide was run into the boat at *a* and phosphoric acid into the wide tube at *b*. On to the apparatus was sealed a mercury manometer, and the whole was held pivoted at *c* so that an up and down movement could be effected as shown by the arrow. The volume of the bulb was a minimum, 30 c.c., so as to maintain the saturated vapour pressure of phosphorus trioxide, and the shaking device prevented film formation on the liquids.

FIG. 1.
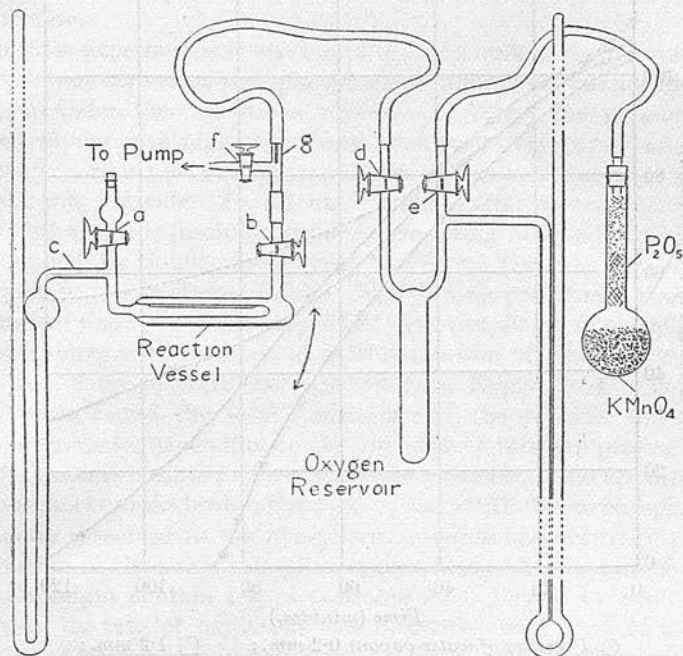
In all experiments the same quantities of liquids were used, *viz.*, 0·2 c.c. of phosphorus trioxide and 8 c.c. of a phosphoric acid solution, a choice which did not introduce a marked change in the pressure of water vapour as the oxide was used up. The apparatus containing phosphoric acid was evacuated, and oxygen, generated by heating potassium permanganate, passed in till its partial pressure was 100—110 mm. After the apparatus had been heated to 25°, liquid phosphorus trioxide was run into the boat and pressure readings were made at intervals. The pressure–time curves (Fig. 2) illustrate the nature of the results.

Experiment 1. When the pressure of water vapour was very

low—0·2 mm.—oxygen was absorbed at a slowly increasing rate until all had gone in $1\frac{1}{2}$ hours. During oxidation, glowing and flashing took place in the vapour phase, the luminescence always tending to be away from the phosphorus trioxide source, *i.e.*, not above the boat. Luminescence was all the time of the same nature, but brighter at lower pressures, and it faded and disappeared abruptly when nearly all the oxygen was used up. Most of the phosphorus trioxide seemed to be oxidised.

Fig. 2.
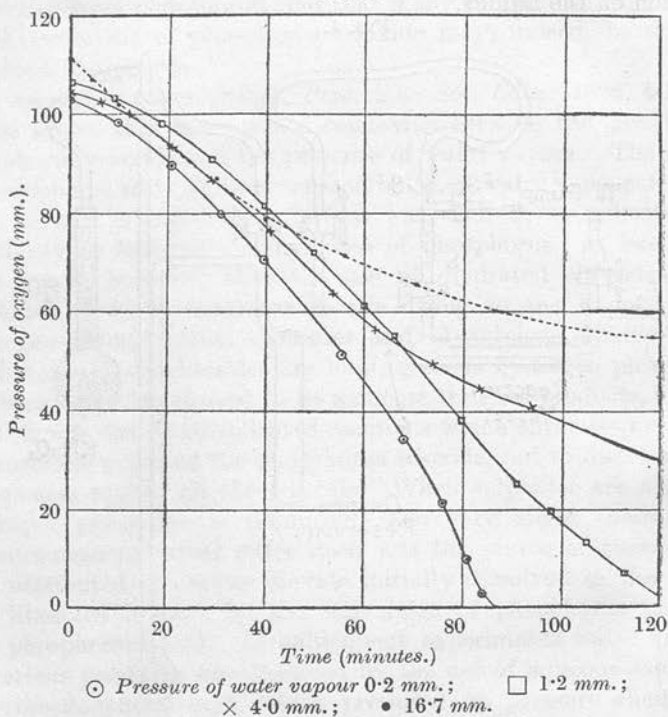
⊙ *Pressure of water vapour 0·2 mm.* ;   □ *1·2 mm.* ;
     × *4·0 mm.* ;   ● *16·7 mm.*

Experiment 2. The rate of absorption of oxygen in presence of 1·2 mm. pressure of water vapour was similar to that in Expt. 1, but the rate fell off after about 70 minutes. The glow phenomena up to this point were also similar, except that glowing took place to a slight extent above the boat. After 90 minutes, when the rate of oxidation was slower, there was permanent glowing round numerous solid particles in the boat. This was not observed when the pressure of water vapour was very low. No phosphorus trioxide remained.

Experiment 3. When the pressure of water vapour was 4 mm. the rate of oxidation for 40 minutes was similar to that in the two

preceding experiments. The glow tended very early to pass above the boat, and steady glowing showed at numerous points in the boat, earlier than in Expt. 2. The passing of the glow to the boat coincided with a reduction in the rate of absorption of oxygen and with the disappearance of phosphorus trioxide.

Experiment 4. With a high pressure of water vapour, flashing occurred after a few minutes above the boat, and in 10 minutes steady glowing took place in the boat. The phosphorus trioxide was practically all used up. After ½ hour the only glowing was that round the solid particles in the boat, and the fairly rapid initial rate of oxygen absorption had given way to a very slow absorption.

In these experiments it was found that the bulk of the phosphorus trioxide was converted into phosphorous acid, which did not absorb oxygen under the conditions prevailing. When the pressure of water vapour was high, this conversion was very rapid, and the subsequent slow rate of oxygen absorption was therefore not due to phosphorus trioxide. In all experiments, after the oxygen was used up, a small, insoluble residue, consisting of minute particles surrounded by liquid, remained in the boat; this was apparently phosphorus, for it glowed in air. The glowing previously observed in the boat was around these particles. As a test, 40 mg. of phosphorus were disintegrated in 2 c.c. of a 50% solution of phosphoric acid and part of the mixture was oxidised as in Expts. 1—4. Glowing took place round the solid ¦particles and the pressure fell at a measurable rate, depending on the quantity of mixture present and on the amount of liquid surrounding the particles. The appearance of phosphorus in the boat in Expts. 1—4 was attributed to phosphorus originally dissolved in the phosphorus trioxide and set free by the conversion of the oxide into phosphorous acid. As the phosphorus trioxide might contain 1% of phosphorus, as judged by results of analysis, its rate of oxidation was compared with that of a 1% solution of phosphorus in paraffin oil. With the latter the pressure of oxygen fell 100 mm. in 3—4 minutes. This rapid rate of oxidation therefore bore no resemblance to the rates found for phosphorus trioxide. Glowing appeared only at the surface of the paraffin solution.

The rate of oxygen absorption by phosphorus trioxide, with low water-vapour pressure, was examined at constant pressure and volume. The boat tube was connected as shown in Fig. 1 with a 45—55 c.c. oxygen reservoir, to which were attached a mercury manometer, reading up to 800 mm. pressure, and a flask in which oxygen was generated by heating potassium permanganate, and dried by passage through a short column of phosphoric oxide.

The boat apparatus was provided with a manometer, registering up to 600 mm. pressure, which on account of its weight was attached at c by means of rubber tubing to the reaction bulb. The latter was moved up and down as before. The boat apparatus and as much as possible of the reservoir were put in a thermostat at 25°. The volumes of the reaction vessel and of the reservoir between b and e were known for all pressures.

In an experiment, the reservoir was charged with oxygen at a pressure about 300 mm. above the constant pressure required; 8 c.c. of a 97% solution of phosphoric acid and 0·5 g. of phosphorus trioxide were run into the reaction bulb and the apparatus was quickly evacuated between a and d. Tap f was closed and oxygen admitted to the evacuated bulb through tap b until the pressure was just below that required. The rate of inflow was controlled by means of the narrow capillary, g. When the apparatus had been 10 minutes in the thermostat, the pressure in the reaction vessel was carefully adjusted to the constant-pressure mark by admitting oxygen from the reservoir. Immediately after closing tap b, the time was noted and the pressure in the reservoir read off. Pressure in the reaction bulb was next allowed to fall not more than 5 mm. and then raised by admission of oxygen to about 5 mm. above the constant-pressure mark. The pressure fell again from this point, and the times of reaching the constant-pressure mark and the pressure of the reservoir were noted. Readings were made at intervals for $1\frac{1}{2}$ hours or until the phosphorus trioxide was exhausted. From the change in PV, the product of the pressure and the volume of the reservoir, the amount of oxygen absorbed in a given time could be determined. For an experiment performed at 25° and at constant pressure (100 ± 4 mm.) the following results were obtained :

t (mins.).	P (cm.).	V (c.c.).	PV.	$(PV)_0 - (PV)_t$ $= (\delta PV)_t$.
0	31·35	50·5	1583	0
7·5	31·0	50·5	1566	17
25	30·15	50·4	1520	63
29·5	29·9	50·4	1507	76
36	29·55	50·35	1487	96
42	29·2	50·3	1469	114
49	28·85	50·3	1451	132
57	28·35	50·25	1425	158
67	27·8	50·2	1395	188
75	27·4	50·15	1374	209
82·5	26·9	50·1	1348	235
90·5	26·4	50·1	1323	260

The change in PV in the time t, $(\delta PV)_t$, was equivalent to the volume of oxygen absorbed (in c.c. at 25° and 1 cm. pressure). Except for a slight initial retardation, the rate of absorption was

practically constant. Experiments performed with the pressure of oxygen constant at 600, 300, 200, and 50 mm. gave results of the same type, but showing different rates of absorption of oxygen. In order to compare the rates, the amount of oxygen absorbed in 60 minutes, $(\delta PV)_{60}$, was determined for each and the corresponding curve constructed (Fig. 3). It was unnecessary to correct for the change in volume of the reaction vessel with pressure, for the reaction only took place in the bulb part, which was the same for all.

An experiment at 25 mm. pressure was unsatisfactory, as the rate of oxidation on two occasions suddenly increased considerably. Fig. 3 indicates that the rate of oxygen absorption may become very great at pressures below 50 mm., an indication, probably, of ignition.

FIG. 3.
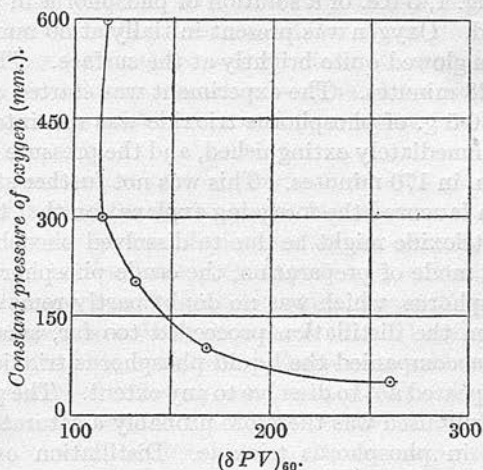
The results, which were all obtained with one specimen of phosphorus trioxide, showed that the rate of absorption of oxygen between 600 and 300 mm. pressure was practically constant but increased regularly as the pressure fell below 300 mm. This bore a resemblance to the rate of oxidation of phosphorus in moderately dried oxygen (see Russell, J., 1903, **83**, 1263).

In all experiments the position of the luminescence was striking. Bright flashing occurred principally below the boat, just above the acid surface, or at the end of the tube beyond the boat, i.e., away from the source of phosphorus trioxide and near the water-vapour source. Attention has already been directed to the appearance of luminescence at sources of moisture at considerable distances from the oxide (Miller, *Proc. Roy. Soc. Edin.*, 1926, **46**, 239). Owing to the ease with which phosphorus trioxide took up water vapour in a

partially evacuated apparatus, it was difficult to imagine that in every instance phosphorus trioxide existed where luminescence appeared. Could the luminescence have been due to dissolved phosphorus ? And if so, why did not luminescence appear at the surface of the liquid oxide as in the case of phosphorus dissolved in paraffin oil ? The only explanation seemed to be that phosphorus trioxide prevented the luminescence of phosphorus. Phosphorus trioxide vapour containing phosphorus would therefore only luminesce if something were present to destroy the phosphorus trioxide. Water vapour, which is essential for the luminescence at the ordinary temperature, has this effect. One would then expect phosphorus trioxide to destroy the glow of slowly oxidising phosphorus. The following experiment was performed. Below the boat of the apparatus in Fig. 1, 5 c.c. of a solution of phosphorus in paraffin oil were introduced. Oxygen was present initially at 50 mm. pressure, and the solution glowed quite brightly at the surface. The pressure fell 29 mm. in 28 minutes. The experiment was started afresh, and after a minute 0·5 g. of phosphorus trioxide was run into the boat. The glow was immediately extinguished, and the pressure afterwards fell only 16 mm. in 170 minutes. This was not further studied, but the observation favoured the foregoing explanation that the glowing of phosphorus trioxide might be due to dissolved phosphorus.

Owing to its mode of preparation, the crude phosphorus trioxide contained phosphorus, which was no doubt partly removed by distillation. When the distillation proceeded too far, small globules of phosphorus accompanied the liquid phosphorus trioxide into the receiver and appeared not to dissolve to any extent. The phosphorus trioxide ordinarily used was therefore probably a saturated solution of phosphorus in phosphorus trioxide. Distillation over copper was not specially effective in removing phosphorus. Analysis, as previously mentioned, suggested the presence in the oxide of 1% of phosphorus. The well-known reddening of phosphorus trioxide in light has also been attributed to dissolved phosphorus. It is significant that the actual extent of decomposition is slight; for instance, Thorpe and Tutton (J., 1891, **59**, 1019) found only 1% of red phosphorus in a sample of oxide exposed for 7 months to light.

In order to determine the part, if any, played by phosphorus in the luminous oxidation of phosphorus trioxide, it was obvious that the preparation of a phosphorus-free oxide was desirable. An unsuccessful attempt was made to dehydrate pure phosphorous acid. In another attempt phosphorus trioxide was exposed to light in an evacuated bulb, and the oxide was volatilised from the red solid at 25° into a second bulb where it was again exposed. Reddening occurred as before and the process was once more repeated. The

reddening effect was purely a superficial one. The light seemed to affect the white, opaque phosphorus trioxide, not the transparent crystals which sometimes formed. If the latter were melted and resolidified, they gave a white opaque solid which was affected by light. As there was apparently no diminution in the amount of reddening in the third bulb, this attempt to separate phosphorus was abandoned.

The next method adopted was the recrystallisation of freshly distilled phosphorus trioxide from a suitable solvent. Carbon disulphide is by far the best solvent for phosphorus but phosphorus trioxide also dissolves readily. A preliminary trial showed, however, that it could be employed if the temperature of recrystallisation was about $-18°$ and the amount used was small. The solvent was dried and distilled over mercury before use. Carbon disulphide is known to be a strong inhibitor of the glow of phosphorus, but it was found that there was no diminution of the glowing of a specimen of phosphorus trioxide after it had been dissolved in carbon disulphide and the solvent removed by evaporation, finally with the aid of a pump.

The Recrystallisation of Phosphorus Trioxide.—As a trial a small quantity of freshly distilled phosphorus trioxide was recrystallised four times from carbon disulphide in an atmosphere of carbon dioxide. The solvent was then expelled by a fairly rapid stream of carbon dioxide, and the purified oxide, about 25% of the original bulk, transferred to a boat apparatus (Fig. 1) and oxidised at 25° in presence of a 97% solution of phosphoric acid and oxygen at a constant pressure of 100 mm. (compare p. 1851). At first no glowing was seen, but after a time there were occasional bright flashes without pressure change in 50 minutes. It was suspected that a trace of carbon disulphide was responsible for the lack of oxidation. The apparatus was therefore re-evacuated and fresh oxygen passed in. Slight glowing occurred and the pressure fall corresponded to $(\delta PV)_{40} = 5\cdot2$. After a further evacuation and addition of oxygen the pressure fall was practically the same. The rate of oxidation of ordinary distilled phosphorus trioxide was previously found to be represented by $(\delta PV)_{40} = 108$ (see table, p. 1852), therefore the rate of oxidation of the purified oxide was reduced to one-twentieth of the original, probably corresponding to a similar reduction in the amount of dissolved phosphorus. The phosphorus trioxide obtained from the mother-liquor was found to oxidise at the normal rate.

These results showed that greater care had to be taken in eliminating solvent from the purified oxide. The apparatus shown in Fig. 4 was designed for recrystallisation experiments. It consisted

of a flat-bottomed tube provided with a side tube through which the mother-liquor from the crystals could be poured. It was further provided with a rubber stopper holding a small tap-funnel, and with a glass rod to which was attached by platinum at the lower end a perforated porcelain disc of nearly the same diameter as the tube. The disc could be moved up and down the tube like a piston. Dry carbon dioxide was passed into the apparatus as shown. Freshly distilled phosphorus trioxide and carbon disulphide were mixed by stirring in the tube and cooled to $-18°$, the perforated disc being moved up and down to prevent formation of crystals

FIG. 4.　　　　FIG. 5.

on the walls. The crystals were then allowed to settle and the disc was pressed down to force out the liquor. The latter was quickly poured off into the side bulb and thence removed. The recrystallisation was repeated and the crystals were finally washed with cooled carbon disulphide. The purified oxide was melted, transferred to a small tube, and solvent removed by evacuation with an oil pump, the oxide meanwhile being many times melted and resolidified. The yield of oxide was slightly higher than before. The specimen glowed when rubbed on the fingers, and in ozonised oxygen, but did not ignite on cotton wool. When oxidised according to the usual method the amount of oxygen absorbed was $(\delta PV)_{40} = 9$, slightly more than before, and there was quite bright flashing at intervals.

The maximum amount of oxygen absorbed by this oxide corresponded to little more than 0.1% of dissolved phosphorus.

Light petroleum (b. p. 40—$60°$) was tried in case the preceding results were due to carbon disulphide. Recrystallisation was effected five times and the solvent removed as before. The amount of oxygen absorbed by a portion of the oxide was equivalent to $(\delta PV)_{40} = 27$, three times the value found above. If the oxidation was due to phosphorus alone, this result indicated that there was three times as much phosphorus left in the oxide as in the preceding experiment and one-quarter of the amount present in the ordinary distilled oxide for which $(\delta PV)_{40}$ was 108. One might expect to obtain identical results for the rate of absorption of oxygen by the three specimens of phosphorus trioxide obtained by saturating the two purified oxides and the unpurified oxide (if not already saturated) with phosphorus at $25°$. For the first two the values of $(\delta PV)_{40}$ were found to be 92 and 90, and for the last, 100. The two lower values were attributed to the fact that only minimum quantities of the solutions were prepared and phosphorus separated slightly while the oxides were being measured out. This did not happen with the third specimen. The value 100 was lower than that previously obtained for phosphorus trioxide, *viz.*, 108. The latter value was due to the use of oxide melted at 30—$40°$, which contained sufficient phosphorus to saturate it at a temperature above $25°$ and more than enough to saturate it at $25°$.

The recrystallisation of a much larger quantity of phosphorus trioxide was attempted. Light petroleum was apparently not so effective as carbon disulphide in removing phosphorus, but it had the advantage that larger quantities could be used. A combination of methods was therefore adopted, the recrystallisation being effected with carbon disulphide and the crystals washed with light petroleum. 40 C.c. of freshly distilled phosphorus trioxide were mixed with one-third of the volume of pure carbon disulphide and recrystallised at $-18°$. The crystals were pressed as free as possible of liquor and washed with 15 c.c. of cooled light petroleum. The process was twice repeated with diminishing quantities of the solvents, and followed by two final washings with light petroleum (5 c.c. and 10 c.c.). The crystals were melted and filtered through glass-wool into a bottle from which air was displaced by dry carbon dioxide. The yield was about one-third of the original bulk.

The oxide in the mother-liquors was recovered, excess of phosphorus removed, and the oxide distilled and recrystallised as before. In all, three products were obtained and put in one bottle from which the remaining solvent was carefully removed as before. The phosphorus trioxide in the last mother-liquor was recovered from

solution in the usual manner and distilled in a vacuum to give a clear phosphorus-saturated solution of phosphorus trioxide.

A little of the purified oxide was oxidised in presence of 4 mm. of water vapour. The total amount of oxygen absorbed corresponded to about 0·02% of dissolved phosphorus. Bright flashing occurred under the boat during the first $\frac{1}{2}$ hour; after 3 hours no glowing was seen and the pressure remained steady. This experiment indicated further removal of phosphorus from the oxide. A drop of this purified material when rubbed on the fingers gave a bright but momentary glow, whereas a drop of the ordinary oxide gave a glow sufficiently bright and lasting to illuminate the whole hand. It was supposed that the purified oxide glowed and absorbed a minute quantity of oxygen because of the retention of a trace of phosphorus. Elimination of this trace by further recrystallisation was impracticable, but it was thought that it might be eradicated by exposure of the oxide to sunlight, a process in which there was no further introduction of substances with an inhibitory effect on the glow. According to expectations the oxide reddened in sunlight, but not to the extent shown by the unpurified oxide. The apparatus shown in Fig. 5 was designed. Initially only that part was used which consisted of the three glass bulbs joined together as indicated. Phosphorus trioxide was drawn into bulb A and x was sealed off. The three bulbs were then thoroughly evacuated and the taps closed. As large a surface as possible of the phosphorus trioxide was exposed to light for a few hours and considerable reddening took place. The apparatus was re-evacuated and the phosphorus trioxide in bulb A volatilised into bulb B by heating A to 40° and cooling B. The oxide was again exposed to light, whereupon further reddening occurred, and then transferred to bulb C for a third exposure. In bulbs B and C the reddening was not so extensive as in bulb A. The second part of the apparatus, which had not been contaminated with phosphorus trioxide vapour containing phosphorus, was now sealed on to the three bulbs, and the tube E charged with phosphoric oxide. The whole apparatus was evacuated and the phosphorus trioxide in bulb C volatilised through the phosphoric oxide into the receiving bulb D. The drying tube and the bulb D were then filled with pure, dry carbon dioxide to atmospheric pressure, and portions of the oxide removed as required.

The Properties of Purified Phosphorus Trioxide.—1. At the ordinary temperature the oxide was a transparent, crystalline solid, lacking the opaque, waxy appearance of the unpurified product, caused probably by the separation of phosphorus from solution, on solidification.

2. A clear, colourless sample of purified phosphorus trioxide

contained in an evacuated bulb was exposed to light for 10 weeks in a well-lit laboratory, but, although it was several times melted and resolidified, it remained colourless and transparent. Crude phosphorus trioxide similarly treated was readily affected by light (see p. 1854). A second sample of purified oxide, which was kept in an atmosphere of carbon dioxide and used for the following experiments, was also exposed to light. The colourless crystalline mass assumed, during the first few hours' exposure, a faint pink tinge which did not deepen on further exposure for 6 weeks. The colour was due to the separation of a very small quantity of red substance.

3. When rubbed on the fingers the purified oxide gave no glow, and for a short time there was a pungent acid smell resembling that of hydrochloric acid. The phosphorus smell so readily detected with ordinary phosphorus trioxide was entirely absent. The pure oxide when spread on cloth did not ignite as does the ordinary product, but when mixed with a small proportion of the crude oxide, or with phosphorus, glowing and ignition were restored.

4. The m. p.'s of the purified and unpurified oxides were determined in a vacuum in small melting-point tubes, the oxide in each case having been initially volatilised through phosphoric oxide. The values found were : Purified oxide, 23·8°; unpurified oxide, 22·4°.

5. In order to obtain an indication of the amount of phosphorus dissolved in the unpurified oxide, the depression constant of the pure oxide was found by determining by Rast's method (*Ber.*, 1922, **55**, 1051) the lowering of freezing point produced by naphthalene as solute. With solutions containing 1·98 and 2·67% of naphthalene the lowerings were 1·85° and 2·4° respectively, giving for the depression constant the values 11,700 and 11,200. For the lowering of freezing point produced by phosphorus, *viz.*, 1·4°, a depression constant of 11,000 gives 1·6 g. as the amount of phosphorus (as P_4) dissolved in 100 g. of trioxide.

6. The pure oxide and the oxide saturated with phosphorus at 25° were analysed quantitatively : 0·15—0·25 g. was melted under water in a small flask and heated at 40—50° till converted into phosphorous acid. The pure oxide left no residue, whereas the unpurified oxide left a residue of phosphorus. An excess of liquid bromine was added and then 3—4 c.c. of 4*N*-sodium hydroxide, since hypobromite is known to oxidise phosphorous acid. Phosphorus was also completely oxidised. After a short time 5 c.c. of concentrated nitric acid were added and the solution was boiled to free it from bromine. The phosphoric acid was precipitated twice as magnesium ammonium phosphate, which was converted into pyrophosphate

(Found, for purified oxide : 100·04, 100·05; for unpurified oxide : 101·37, 101·47%). On the assumption that the purified oxide was entirely free from phosphorus, the last two results correspond respectively to 1·74 g. and 1·87 g. of free phosphorus in 100 g. of trioxide.

7. The solubility of phosphorus in the purified oxide at 25° was determined by shaking a weighed excess of purified phosphorus with about 1 g. of phosphorus trioxide in a small stoppered tube, in an atmosphere of carbon dioxide. The tube was first heated sufficiently to melt the phosphorus and then allowed to stand at 25°. The excess of phosphorus collected into a globule which was easily removed, washed, and weighed. The weight of phosphorus dissolved corresponded to 1·71 g. per 100 g. of trioxide. Experiments 5, 6, and 7 therefore showed satisfactory agreement.

8. The behaviour of the purified oxide in oxygen was studied. At 25° and in presence of 4 mm. of water vapour, the oxide neither glowed nor absorbed oxygen at 100 mm. or 18 mm. pressure, in contradistinction to the absorption of oxygen, accompanied by luminescence, exhibited by impure phosphorus trioxide (see Expt. 3, p. 1859). In presence of concentrated sulphuric acid it gave no deposition of oxides at 25° in oxygen at 600 mm. pressure, whereas unpurified phosphorus trioxide, under similar conditions, deposited phosphorus tetroxide (see Miller, *Proc. Roy. Soc. Edin.*, 1926, **46**, 239). At higher temperatures, the following phenomena were noticed. 0·2—0·3 G. of oxide was mixed with phosphoric oxide and volatilised into a 6 c.c. bulb into which pure dry oxygen was passed to a pressure of 300 mm. The bulb was sealed and heated gradually, but no glowing or fuming was seen below 200°. At about 220°, fuming was observed, accompanied by a very faint glow. The action was not brisk, for after $\frac{1}{4}$ hour's heating at this temperature oxygen was still present. With undried phosphorus trioxide and moist oxygen the result was much the same, but in a second similar experiment oxidation appeared at 130°. Unpurified phosphorus trioxide gave an entirely different result, igniting at 40° in dry oxygen at 300 mm. pressure and using up all the oxygen. When ozonised oxygen containing 1% of ozone was passed at a slow rate over the pure phosphorus trioxide at 25°, oxidation occurred without luminescence. Under similar conditions, ordinary phosphorus trioxide glowed brightly and difficulty was experienced in preventing ignition.

9. When the purified oxide was melted under excess of water and heated gradually, it was simply converted into phosphorous acid, until a temperature of 75—80° was reached. At this point decomposition set in, bubbles of gas passed up through the water

from the oxide, and yellow and red solid products were formed. The gas fumed at the surface of the water and gave bright flashes. Unpurified phosphorus trioxide exhibited the same phenomena at a somewhat lower temperature.

When purified phosphorus trioxide in excess was sealed in an evacuated bulb with a small quantity of water, a clear yellow syrup formed, which after several days became opaque. The bulb was opened under water, but no gas was present. The amount of yellow solid was so small that accurate analysis was impossible— it is possibly a suboxide.

10. When the purified oxide was heated in a vacuum at 300°, red, yellow, and white decomposition products were formed, phosphorus tetroxide being amongst them. The thermal decomposition of ordinary phosphorus trioxide gives a similar result.

11. A portion of the pure trioxide was saturated with purified phosphorus at 25°. The oxide so obtained assumed on solidification the white, opaque appearance of unpurified phosphorus trioxide, glowed in air, ignited on cloth, and reddened in light.

Summary.

A study of the rate of absorption of oxygen by phosphorus trioxide in presence of water vapour at various pressures led to the conclusion that the luminescence of the oxide was essentially connected with the presence of dissolved phosphorus.

Phosphorus trioxide, as prepared by Thorpe and Tutton's method, invariably contained phosphorus, the bulk of which could be removed by several low-temperature recrystallisations from carbon disulphide. The remainder was removable by exposure of the oxide to light and subsequent volatilisation from the red product.

The pure oxide so obtained melted at 23·8°, *i.e.*, 1·4° higher than the unpurified product, and lacked many of the properties formerly attributed to phosphorus trioxide. For instance, it neither glowed nor oxidised in moist or dry oxygen at the ordinary temperature and was unaffected by sunlight. When it was heated in a sealed bulb with dry oxygen at 300 mm. pressure, fuming and very faint glowing were observed at about 200°. By addition of pure phosphorus to the pure oxide the properties previously regarded as characteristic of phosphorus trioxide were restored.

The trioxide was found to dissolve 1·7 g. of phosphorus per 100 g. when saturated at 25°.

It is not yet known if the absorption of oxygen by the impure oxide is due to phosphorus alone or to phosphorus and phosphorus trioxide together, but this point is being investigated.

A study of the oxidation products of phosphorus in oxygen and

of phosphorus trioxide in oxygen and ozonised oxygen is being continued.

The Slow Oxidation of Phosphorus Trioxide. Part I. The Action of Water - Vapour on Phosphorus Trioxide.

By Christina Cruickshank Miller, B.Sc., Ph.D.

IX.—The Slow Oxidation of Phosphorus Trioxide. Part I. The Action of Water-Vapour on Phosphorus Trioxide. By Christina Cruickshank Miller, B.Sc., Ph.D., Carnegie Research Fellow. *Communicated by* Sir JAMES WALKER, F.R.S. (With four Figures in the Text.)

WHEN phosphorus oxidises slowly in air or oxygen it is commonly supposed to do so in two stages: first, oxidation to trioxide without glow; second, oxidation of trioxide to pentoxide with glow. The object of the present investigation was to study the second reaction with a view to explaining the phenomena associated with the slow oxidation of phosphorus.

Thorpe and Tutton[*] showed that phosphorus trioxide is oxidised with emission of light. Jungfleisch,[†] and subsequent investigators,[‡] attributed the luminescence of phosphorus entirely to the second reaction, namely, the oxidation of phosphorus trioxide. The glow in the case of phosphorus trioxide is not, in general, as brilliant as that observed with phosphorus itself, although the vapour pressure of phosphorus trioxide is greater at a given temperature; neither is the glow generally situated near the surface of the solid, as it is with phosphorus. This would seem to render the above supposition unlikely. We may, however, take into consideration that molecules of phosphorus trioxide produced by the first oxidation of phosphorus are possibly activated, and would consequently react more briskly with oxygen to produce phosphorus pentoxide than would vapour derived directly from phosphorus trioxide. More recently, Downey[§] has demonstrated that light from oxidising phosphorus trioxide like that from phosphorus is capable of ionising oxygen, and H. J. Emeléus[||] has established the identity of the spectra. In addition Emeléus has found that phosphine burning in air at reduced pressure gives the same spectral bands. Rinde[¶] has suggested that

[*] *Journ. Chem. Soc.*, **57**, 545, 1890.   [†] *Comptes Rendus*, **140**, 444, 1905.
[‡] Schenck, *Mihr and Bantlien*, *Ber.*, **39** (2), 1506, 1906 ; Scharff, *Zeit. f. phys. Chem.*, **62**, 179, 1908 ; L. and E. Bloch, *Comptes Rendus*, **147**, 842, 1908 ; Weiser and Garrison, *Journ. Phys. Chem.*, **25**, 349, 473, 1921 ; Gilchrist, *Proc. Roy. Soc. Edin.*, **43** (2), 197, 1923.
[§] *Journ. Chem. Soc.*, **125**, 347, 1924.
[||] *Ibid.*, **127**, 1362, 1925.
[¶] *Arkiv Kemi. Min. Geol.*, **7**, No. 7, 1917.

in dry oxygen phosphorus trioxide is directly oxidised to pentoxide without glow, but that in moist oxygen an intermediate compound, possibly phosphine, is formed which oxidises with glow.

The present investigation, which was begun in October 1924, and prior to the publication of Emeléus's paper, was being primarily pursued in two directions:

1. Photography of the spectrum of phosphorus trioxide.

2. The effect of moisture on phosphorus trioxide.

After Emeléus's results were published the former branch was discontinued and the latter systematically studied.

Phosphorus trioxide was prepared by Thorpe and Tutton's method, the average yield being 5 grams from 70 grams of phosphorus. A clear, colourless liquid was obtained by distilling the crude trioxide at 30 mm. pressure. It solidified at ordinary temperature and melted sharply at 22·5° C. Analysis of a sample was conducted in the following manner :—

A weighed quantity (about 0·5 gram) of phosphorus trioxide in a small tube was dropped into a 50 c.c. Kjeldahl flask containing a few cubic centimetres of chloroform. After addition of 20 c.c. of water, bromine in chloroform was slowly added until the chloroform layer retained a brown colour. The chloroform was boiled off, and the aqueous solution boiled until colourless with 1–2 c.c. of concentrated nitric acid. After cooling, the solution was made up to 100 c.c., and 20 c.c. used for each analysis. The liquid was made slightly alkaline with ammonia, and the phosphate estimated as magnesium pyrophosphate by the method given in Classen's *Quantitative Analyse*, p. 67. Three analyses gave for the percentage purity of the trioxide the values 100·3, 100·2, and 100·5.

During the experiments directed to the photography of spectra a method was found for fixing the position of the trioxide glow for considerable lengths of time. A description of the most satisfactory experimental arrangement is given below as the effect of moisture is thereby well illustrated.

The apparatus used is shown in fig. 1 on the next page. Air, dried by concentrated sulphuric acid, was passed at low pressure, 10–12 mm., through a tube on the upper wall of which was solid phosphorus trioxide. Thence it passed into a wide tube (4 cm. diameter) which was closely packed with undried, or even slightly damp, cotton-wool. The latter reached as far as a capillary of 1·5 mm. diameter. Here, at (*a*), immediately beyond the cotton-wool, a small, bright, steady glow estab-

lished itself, remaining in position for twelve hours and sometimes twenty-four. Provided that no small crevices were left in the cotton-wool plug no glowing occurred save at the capillary. The effect was, no doubt, associated with the water-vapour removed by the gas stream from the cotton-wool, as dried cotton-wool was without action. When, presumably, all moisture had been removed from the plug, the glow frequently rushed suddenly from the capillary and could not be restored to its original position.

The experiments described below likewise indicated a connection between glowing and the presence of water-vapour.

Experiment A.—In a closed vertical tube (2 cm. diameter) filled with undried oxygen at atmospheric pressure, and containing at the foot a small quantity of phosphorus trioxide, flashing was observed to proceed regularly at the rate of one flash in five minutes, at 15°. After a flash, which occurred about half an inch above the trioxide, a cloud of minute particles, probably
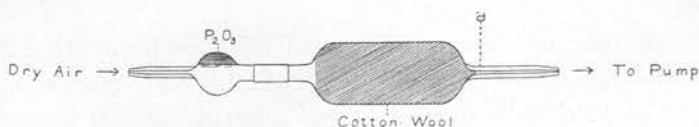

Fig. 1.

of phosphorus pentoxide, was observed to fall, leaving a faint haze behind. The next flash occurred immediately above this haze, the height of which was thereby increased. In one and a half hours the upward advance of the haze was one inch. The occurrence of flashing at ever-increasing distance from the trioxide was attributed to the gradual absorption of moisture by the phosphorus pentoxide formed in the oxidation process in the lower part of the tube.

Experiment B.—A slow, steady stream of dry air at 15 mm. pressure was passed over phosphorus trioxide, and then into a long tube, 1 cm. wide, containing five loosely fitting rolls of moist filter-paper ranged four inches apart. A glow was made to settle, with slight adjustment of the air-current, in and above the first roll, and remained fairly steady for fifty minutes. The glow then moved along the tube attaching itself in turn to each of the rolls for five, ten, fifteen, and twenty minutes respectively, and finally left the tube. The rolls of paper were examined after the experiment and found to be dry. Evidently a glow only settled near a roll of filter-paper when the latter was moist, and moved away when the dry air-current and the phosphorus pentoxide produced in the oxidation had used up all the moisture.

The foregoing observations, in conjunction with some peculiar pressure-time relations in the oxidation of phosphorus trioxide in presence of moisture, led to a fuller investigation of the effect of water-vapour on phosphorus trioxide.

Water-vapour at various pressures was allowed to react at 25° with phosphorus trioxide in evacuated bulbs of the type shown in fig. 2.

Into one end of a bulb, constructed from 2 cm. wide glass tubing, was sealed a glass boat. Liquid phosphorus trioxide was later run into the boat, and thereby extended from one end of the apparatus to the other without coming in contact with solids placed in the surrounding tube beneath. Pressure changes in the apparatus were recorded by means of a mercury manometer sealed on
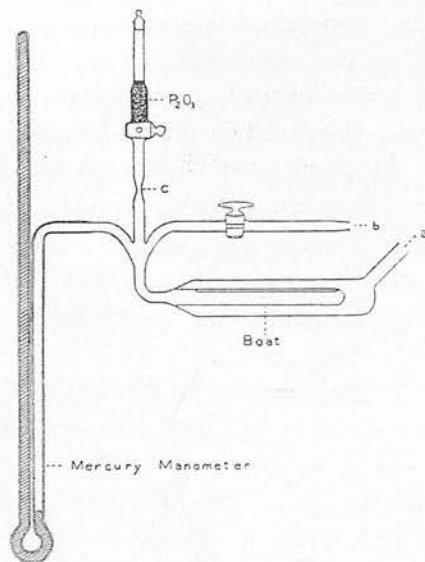

FIG. 2.

to the bulb. Definite pressures of water-vapour were maintained by the use of salt hydrate mixtures, namely :—Na_2SO_4, 10 $H_2O + Na_2SO_4$, 18 mm.; $BaCl_2$, $2H_2O + BaCl_2$, H_2O, 5 mm.; $BaCl_2$, $H_2O + BaCl_2$, 2·5 mm.; $MgSO_4$, $H_2O + MgSO_4$, 1·0 mm., all at 25°. Mixtures of sulphuric acid and water, which have been used for a similar purpose, were not here available, since phosphorus trioxide acts on sulphuric acid of 50 per cent. concentration and over, with production of sulphur dioxide. In the case of the first and third hydrate mixtures it was found, with the aid of the differential tensimeter, that the equilibrium pressures of water-vapour were reached in ten minutes. The vapour pressure of phosphorus trioxide at 25° is 3 mm.

About 6 grams of a hydrate were finely ground in a mortar with 1 gram of anhydrous salt, or a lower hydrate, in order to secure by their intimate contact rapid pressure equilibrium with the water-vapour, and the mixture added to the bulb at (*a*) which was then sealed off. The apparatus was evacuated at (*b*) by a Cenco Hyvac pump, and placed in a thermostat at 25°. 0·5–1·0 gram of phosphorus trioxide was run into the boat, (*c*) sealed, and pressure-time changes forthwith noted. The graphs in fig. 3 illustrate the nature of the results. Each curve is numbered to correspond with the experiments detailed in Table I,

page 81, and alongside the number is given the pressure of water-vapour associated with the hydrate mixture used. In experiment III the tube instead of being evacuated contained nitrogen at a pressure of 105 mm. This amount was deducted from all the observed pressure values before the curve was drawn. Experiment I was performed with 5 c.c. of water instead of a hydrate mixture, the vapour pressure being 23 mm. Curve VI is referred to later.

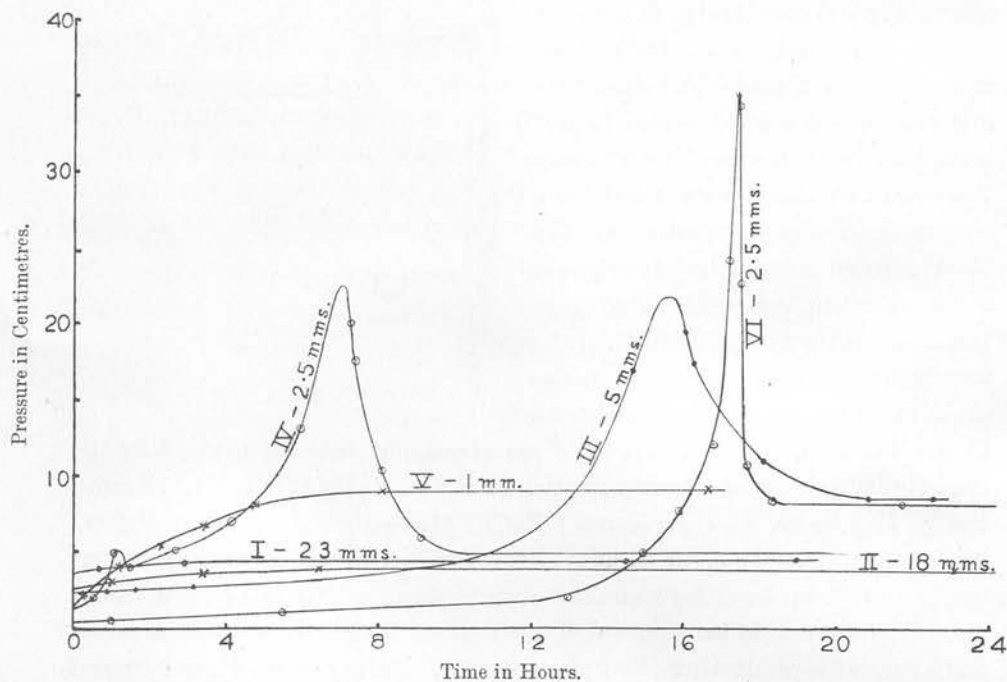In every case it may be noted that a rise of pressure occurs, the

Fig. 3.

rise being slight where the pressure of water-vapour is high. The curves for experiments III and IV, which are associated with the intermediate values of water-vapour pressure, are peculiar in that, at a certain point, a rapid pressure increase ensues, and is succeeded by as rapid a fall.

In bulbs III and IV large quantities of a yellow solid were formed. The rapid pressure increase in experiment IV occurred after the walls of the bulb were covered with a colourless liquid. At the maximum pressure the liquid assumed a yellow tinge and later, as pressure fell, it had a cloudy yellow appearance. After a time the walls of the bulb were entirely covered with yellow solid. The effects were not attribut-

able to the action of light, as similar results were obtained in a dark room. The solid was thought to be solid phosphuretted hydrogen, but, although it responded to some of the tests for the latter, it was only slightly soluble in liquid white phosphorus and did not ignite even at 250° in an open tube. Some white, feathery crystals melting at about 70° were observed on the walls of bulbs III and IV. They were doubtless crystals of phosphorous acid (M.P. 70·1°). Only very small quantities of yellow solid were found in bulbs I and II where aqueous solutions of acid were formed in the boats. Some white, plastic solid produced in experiment I glowed in air and was found to contain a little phosphorus. In bulb V where the vapour pressure of water was low a minute quantity of syrupy liquid, which later became yellow, was produced.

The reactions in the bulbs were not accompanied by luminescence.

When pressure in the five bulbs ceased to alter, the gas contents were removed by means of a Töpler pump, and analysed over mercury in small absorption pipettes constructed for the purpose.   Two measuring burettes were employed, one, a capillary burette similar to that designed by Reeve,* the other, a larger modification for gas volumes up to 5 c.c.   It was supposed that phosphine was mainly responsible for the pressure changes, as a small amount of gas which on one occasion accidentally escaped was spontaneously inflammable in air.   The gases were accordingly treated with sodium hypochlorite solution, which readily absorbs hydrides of phosphorus. The results of analysis are given in Table I.   The residues which were

TABLE I

Experiment.	Pressure of Water.	Volumes Analysed.	Per cent. Phosphine.
	mm.	c.c.	
I	23	0·83	89
II	18	0·27	92
III	5	4·00	>90
IV	2·5	1·95	98
V	1·0	1·63	98

small were not further analysed. The figures show that phosphine was the essential constituent of the residual gases. Confirmation of this was afforded by the easy inflammability of the gas, and the formation of a black precipitate with ammoniacal copper sulphate solution.

* *Journ. Chem. Soc.*, **125**, 1946, 1924.

The production of phosphine from phosphorus trioxide and water
vapour has not hitherto been demonstrated at low temperature, although it
is known that spontaneously inflammable phosphine is one of the products
of interaction of the trioxide and hot water. That phosphine may be
associated with the glow phenomena of phosphorus has been suggested by
Gmelin,* Rinde,† and Eméléus.‡

Experiment IV was repeated in order to investigate the gases present
at the maximum pressure. When this pressure, 158 mm., was attained the
bulb, of which the walls were covered with colourless liquid droplets, was
cooled to $-16°$, the pressure falling rapidly to 34 mm. The gases were
removed by the Töpler pump, but pressure in the apparatus did not fall
below 12 mm., thus indicating the presence of volatile liquid. On this
occasion the gases reacted in the pump with the mercury, or a dissolved
impurity, giving a black deposit. 90 per cent. of the gas was absorbed by
the hypochlorite solution.

The liquid in the bulb did not solidify, and when the bulb was reinserted
in the thermostat pressure rose to 160 mm. and then fell to 5 mm. The
pressure at the maximum was evidently principally due to the vapour of a
liquid of low boiling point, in all probability the liquid hydride of
phosphorus, which boils at 57–$58°$ at 735 mm. pressure.

An attempt was made to identify the volatile liquid by finding its
vapour pressure at various temperatures below that of the experiment.
To do this it was necessary to determine the pressure due to permanent
gas, that is, gas which could not be condensed at $-20°$.

In order to form more of the liquid, double quantities of the reactants
were used in an experiment which was performed at $28°$. Thirteen hours
elapsed before pressure began to rise appreciably, but after that the rise
was extremely rapid. [See curve VI, fig. 3.] At 351 mm. the bulb was
suddenly cooled from $28°$ to $-18°$. On placing it in the thermostat again
the pressure recorded was 100 mm. higher than before, but after again
cooling and heating no change in the maximum, 437 mm., occurred. The
increase was due to further formation of vapour and gas. The bulb was
once more speedily cooled, and pressure readings taken at various tem-
peratures between $-13°$ and $28°$. The results are given in Table II. On
the assumption that the volatile liquid was liquid phosphorus hydride
boiling at $57.5°$ at 735 mm. pressure, its vapour pressure was calculated
roughly at different temperatures by means of the Ramsay-Young Boiling

---

* *Handbook of Chemistry*, vol. ii (1849), p. 138.
† *Loc. cit.*, p. 20.
‡ *Loc. cit.*, p. 1367.

Point Law, $\dfrac{T_a}{T_b} = \dfrac{T_a^1}{T_b^1}$ where T_a and T_b are the boiling points (absolute scale), of two liquids A and B at a certain pressure, and T_a^1 and T_b^1 their boiling points at another pressure. Chloroform (B.P. 60·2° at 735 mm.) was taken as comparison liquid. The calculated vapour pressures of liquid phosphorus hydride are given in the second last column of the table. The value at $-13°$ was taken to be correct, so that the pressure due to permanent gas at $-13°$ was known and could be calculated for the higher temperatures with the aid of the gas laws. By subtraction of these values from the total pressure the pressure due to vapour was derived. The results are given in the last column of the table.

TABLE II

Temp.	Vol. c.c.	Press. mm. $P_2O_3+H_2O$.	Obs. Press.	Press. $PH_3+P_2H_4$.	Press. PH_3, calc.	V.P. $CHCl_3$.	V.P. P_2H_4, calc.	V.P. P_2H_4, found.
$-13°$	35·5	0	208	208	175	29	33	33
$0°$	35·9	0	268	268	182	61	70	86
$5·5°$	36·2	1	296	295	184	81	91	111
$11°$	36·4	2	325	323	186	105	116	137
$16°$	36 5	3	348	345	189	129	146	156
$28°$	37·3	6	437	431	193	219	247	238

The values derived in the last column vary in a manner suggestive of a liquid boiling at a slightly lower temperature than chloroform. The vapour pressure may, therefore, be attributed to liquid phosphorus hydride. Hence gaseous and liquid hydrides of phosphorus are produced under certain conditions by the interaction of phosphorus trioxide and water at low temperature.

When pressure decreased rapidly from the maximum both permanent gas and vapour were found to disappear. The following experiment was performed to ascertain whether the gas and vapour interacted, or whether a reaction with water or phosphorus trioxide occurred.

Three vessels of the usual type were sealed together as shown in fig. 4. Bulbs (1) and (3) contained hydrate mixture as previously used in experiment IV, but (2) was empty. After evacuation of the whole apparatus the taps (a) and (b) were closed, and phosphorus trioxide run into bulb (1), in which reaction was allowed to proceed normally to the maximum pressure. When that pressure, 276 mm., had been attained, taps (a) and (b) were momentarily opened to equalise pressure throughout the apparatus. The subsequent pressure changes in the three bulbs are recorded in Table III.

TABLE III

Time in Minutes.	Pressure (mm.).		
	(1)	(2)	(3)
0—Before (a) and (b) opened .	276	2·5	4·5
0—After (a) and (b) opened .	144	142	142
3	142·5	142	135
6	132	142	132·5
34	67	148·5	125
75	54	154	124

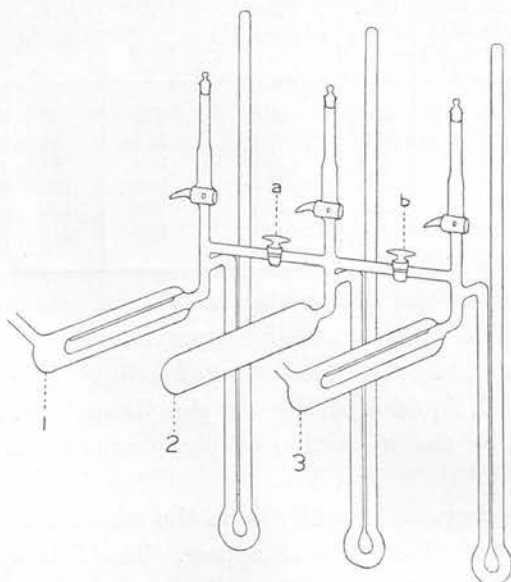The slight pressure fall in bulb (3) bears no resemblance to the usual rapid change. After twelve hours the pressures were unchanged,

FIG. 4.

and when the bulbs were cooled to −16° the decreases were almost in accordance with the gas laws. Hence the pressures were principally due to permanent gas. 0·1–0·2 gram of phosphorus trioxide was run into bulb (2). The effect was instantaneous, pressure falling in two and a half minutes to a steady value, 28 mm. This residue was not due to disappearance of the trioxide and consequent cessation of reaction, for, on momentarily opening tap (b) so that gas from bulb (3) passed into bulb (2), pressure in the latter rose to 74 mm. and then rapidly fell. The rapid pressure decrease from the maximum was therefore due to

interaction of hydrides of phosphorus and phosphorus trioxide. A study of several experiments revealed that there was no obvious connection between the amounts of phosphine and liquid phosphorus hydride which had disappeared during the fall to constant pressure.

Pure phosphine, prepared by dropping a solution of caustic potash on phosphonium iodide, did not react with phosphorus trioxide in a dry bulb, and, on adding water, only a slight pressure decrease occurred. After about a week, however, the walls of the bulb were entirely covered with the yellow solid so often observed. This pronounced effect was not observed when nitrogen replaced phosphine. Further investigations of the yellow solid are being made.

SUMMARY.

1. During spectroscopic investigations of the phosphorus trioxide glow a method was found for maintaining a stationary glow for twelve to twenty-four hours.

2. Experiments were performed illustrating the necessity of water-vapour for the glow phenomena.

3. The effect of water-vapour on phosphorus trioxide in evacuated bulbs was systematically studied at 25°. Pressures of water-vapour ranging from 1–23 mm. were maintained by the use of certain salt hydrate mixtures, and of water.

4. In every case pressure increased owing to the production of phosphine.

5. When the pressure of water-vapour was 2·5 or 5 mm. a liquid, in addition to gas, was produced in sufficient quantity, after the elapse of several hours, to cause a rapid pressure rise to a maximum. Its vapour-pressure at different temperatures showed that it was liquid phosphorus hydride. A rapid pressure fall from the maximum was observed, and was due to the interaction of hydrides of phosphorus and phosphorus trioxide.

The Slow Oxidation of Phosphorus Trioxide. Part II. The Production of Phosphorus Tetroxide by Direct Oxidation of Phosphorus Trioxide.

By Christina Cruickshank Miller, B.Sc., Ph.D.

XXI.—The Slow Oxidation of Phosphorus Trioxide. Part II. The Production of Phosphorus Tetroxide by Direct Oxidation of Phosphorus Trioxide. By Christina Cruickshank Miller, B.Sc., Ph.D., Carnegie Research Fellow. *Communicated by* Sir JAMES WALKER, F.R.S. (With Two Figures in the Text.)

ALTHOUGH the luminescent oxidation of phosphorus trioxide has been frequently studied during the past thirty-six years,[*] comparatively little attention has been paid to the products of the reaction. Indeed it seems that the oxidation of phosphorus trioxide to phosphorus pentoxide has been assumed without proof. The object of this paper is to show that, under certain conditions, phosphorus trioxide is not converted by slow oxidation into phosphorus pentoxide, but into the lower oxide, phosphorus tetroxide, P_2O_4.

In a previous communication [†] the necessity of water-vapour for the glow phenomena was indicated. Since then the rate of oxidation of phosphorus trioxide at 25°, in presence of varying amounts of water-vapour, has been studied. Details of these experiments and the numerical data relative thereto will be published later. The chief points of interest, as far as the present paper is concerned, are that (a) when moisture was excluded from the apparatus, by replacing the source of water-vapour by phosphorus pentoxide, only a very small quantity of oxygen was absorbed even after three months; (b) when the pressure of water-vapour was high, the bulk of the trioxide was converted into a solution of phosphorous acid which did not absorb oxygen; (c) when the pressure of water-vapour was low, such as that derived from a 98 per cent. aqueous solution of phosphoric acid, some solid phosphorous acid was formed near the trioxide, and at that part of the apparatus where glowing occurred a white solid was deposited. This latter solid was not unnaturally thought to be phosphorus pentoxide. The continuance of glowing, however, in close proximity to it was difficult to reconcile with the fact that phosphorus pentoxide abolishes both luminescence and oxidation. On account of the deliquescent nature of the substance

---

[*] Thorpe and Tutton, *Journ. Chem. Soc.*, **57**, 545, 1890 ; Schenck, Mihr, and Banthien, *Ber.*, **39** (2), 1506, 1906 ; Scharff, *Zeit. f. phys. Chem.*, **62**, 179, 1908 ; Rinde, *Arkiv. Kemi. Min. Geol.*, **7**, No. 7, 1917 ; Weiser and Garrison, *Journ. Phys. Chem.*, **25**, 349, 473, 1921.

[†] *Proc. Roy. Soc. Edin.*, **46** (1), 76, 1926.

it could not be removed unchanged from the tube, but it was found that it was not phosphorous acid which melts at 70°, and that it sublimed completely when the tube was heated with a small flame. These observations did not preclude the possibility of its being phosphorus pentoxide which sublimes somewhat readily, and special arrangements had to be made to trap the oxidation product for the study of its properties. In particular, precautions were necessary to prevent interaction with water-vapour.

In a glass tube, 8 inches long and 1 inch in diameter, fixed horizontally, were placed two glass boats—one, 3 inches long, containing phosphoric acid solution (98 per cent.), the other, 1 inch long, containing phosphorus trioxide. In oxygen at 125 mm. pressure oxidation occurred readily, and on the boats and walls of the tube a white solid was deposited. As, however, the experiment was continued too long the deposit was partly acted on by water-vapour. The aqueous solution reduced silver nitrate and mercuric chloride solutions, thus showing that it was not composed entirely of phosphorus pentoxide.

The experiment was repeated with sulphuric acid (98 per cent.) replacing the phosphoric acid, and a boat containing phosphorus pentoxide was placed in one half of the tube. At 25°, and with oxygen at 450 mm. pressure, a pure white solid uncontaminated with water was obtained. The pressure of water-vapour must have been very small, less than ·1 mm. Dry air was added to atmospheric pressure, the boats withdrawn, and the tube evacuated thoroughly. The white solid remained unaltered in bright sunlight, and on heating to 100°, but it sublimed completely at a temperature below 200°. It was thus suspected to be phosphorus tetroxide, a substance first prepared by Thorpe and Tutton* by the thermal decomposition of phosphorus trioxide.

The next step was to analyse the substance quantitatively, a difficult matter owing to the smallness of the quantity usually available and the readiness with which it absorbed moisture. The apparatus shown in fig. 1 was devised for collecting the deposit in a manner suitable for weighing.

The outer vertical tube was widened at the bottom and into this part fitted a weighed tube, 1½ inches long, which was of the same diameter as the upper portion of the long tube. Sulphuric acid (98 per cent.), as source of water-vapour, was contained in a short, perforated test-tube provided with a wick of glass wool to increase the acid surface. A tiny tube with about ·2 gm. of phosphorus trioxide was suspended

* Journ. Chem. Soc., 49, 833, 1886.

below the acid tube.   Dry oxygen, generated by heating potassium permanganate, was passed into the tube to a pressure of about 600 mm. (a perfectly arbitrary choice), and the tube placed in a thermostat at 25° for one or two days.   After that time the walls of the outer and inner tubes and the bottom of the weighed tube were covered with a light, snow-like solid.   As much as possible of the solid was shaken down into the weighed tube.

Pressure in the apparatus was brought to atmospheric by the entry of dry air.   After speedy withdrawal of the acid and trioxide tubes the apparatus was thoroughly evacuated to remove trioxide-vapour, and pressure again restored to normal with dry air.   The lower stopper
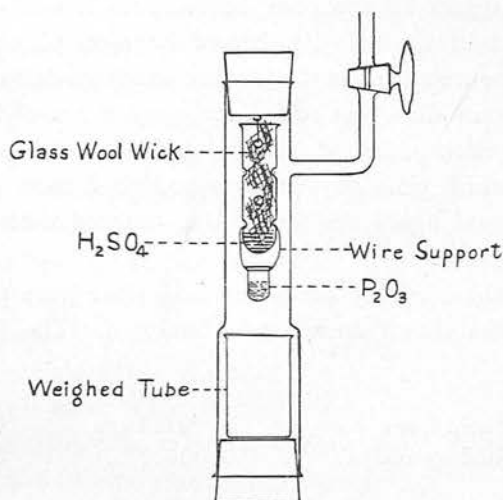

Fig. 1.

was carefully removed and the inner tube dropped into a weighing bottle which was immediately closed and weighed.   It was proposed to estimate the reducing power of the solid as well as the percentage of phosphorus it contained.

The method of estimating the reducing power was as follows:—In order to ensure complete oxidation of the solid it was advisable to use a strong oxidising agent such as bromine.   According to Thorpe and Tutton,* phosphorus tetroxide is decomposed by water into a mixture of phosphorous and phosphoric acids—

$$P_2O_4 \xrightarrow{\quad H_2O \quad} H_3PO_3 + H_3PO_4.$$
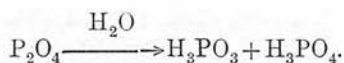
The oxidising agent must, therefore, be such as will convert H_3PO_3 into

* *Loc. cit.*, p. 838.

H_3PO_4. Now Manchot and Steinhäuser * have shown that bromine, in presence of hydrochloric or sulphuric acid, does not oxidise phosphorous acid completely, but that in presence of sodium bicarbonate immediate oxidation occurs. This suggests that the active oxidising agent is sodium hypobromite. After the performance of numerous preliminary experiments a standard solution of potassium bromate was utilised as follows for the oxidation.

To a solution containing less than ·05 gm. of phosphorous acid were added 2 c.c. of each of N.KBrO₃, N.KBr, 2N.HCl solutions. Ten minutes was allowed for complete liberation of bromine which was then converted into hypobromite by means of 4 c.c. of 2N.NaOH solution. For immediate and complete oxidation of the phosphorous acid it was essential to have the latter present in the solution before addition of the alkali. As a precautionary measure an interval of ten minutes was given for oxidation. Excess of potassium iodide was added, and then 6 c.c. of 2N.HCl solution to liberate the bromine which at once reacted with the iodide. After ten minutes, during which time any bromate produced from the hypobromite would be decomposed again, the iodine was titrated with a ·02N solution of sodium thiosulphate.

As a test of the accuracy of the method some pure phosphorous acid prepared by Grosheintz's † method was analysed. The following results were obtained:—

	(1)	(2)
Weight of acid taken . . .	·0444 gm.	·0257 gm.
„ found by analysis . .	·0441 „	·0260 „

The supposed phosphorus tetroxide was estimated in the same way as the phosphorous acid, the solid being first decomposed with a little water. In order to avoid unnecessary dilution, oxidation was effected in the original weighing bottle. Blank experiments were in every case performed to find the thiosulphate equivalent of the bromate used. After titration with thiosulphate the total phosphorus in the oxidised solution was estimated. Slight excess of concentrated nitric acid was added, and the liquid was boiled to expel iodine and bromine, and to concentrate the solution. The liquid was made alkaline with ammonia and the phosphorus estimated, according to the method given in Classen's *Quantitative Analyse*, p. 67.

* *Zeit. f. anorg. Chem.*, **138**, 304, 1924.
† *Bull. Soc. Chim. de Paris*, **27**, 433, 1877.

RESULTS OF ANALYSIS.

	(1)	(2)	(3)
Weight of solid taken	·0162 gm.	(·0184 gm.)*	·0113 gm.
Weight of P_2O_4 calculated from Br_2 absorption	·0171 ,,	·0163 ,,	·0115 ,,
Weight of P_2O_4 calculated from $Mg_2P_2O_7$.	·0161 ,,	·0162 ,,	·0114 ,,

The above results show that the solid consisted entirely of phosphorus tetroxide.

Further proof that the oxidation product was phosphorus tetroxide was obtained. Slight fuming occurred when the substance was decomposed by water, and the aqueous solution responded to the tests applied by West † to phosphorus tetroxide. The solid could be obtained in crystalline form by careful sublimation of the snow-like deposit in an evacuated tube. The crystals, which were colourless, transparent, and highly lustrous, were submitted to microscopic examination. They were cubical in shape, but did not belong to the regular system as they were highly birefringent.

In order to compare the crystal form with that of phosphorus pentoxide some of the latter was sublimed in an evacuated tube. In fig. 2 the crystal habits of the two substances are shown.

(a)   (b)

P_2O_4 P_2O_5

FIG. 2.

The crystallographic features of the supposed phosphorus tetroxide were in agreement with Thorpe and Fletcher's ‡ observations on phosphorus tetroxide. It is interesting that no crystals like those in (b) were observed in the tube containing the deposit. The conditions under which phosphorus trioxide and phosphorus tetroxide oxidise to phosphorus pentoxide have still to be found.

Preliminary investigations have been made in the case of the slow oxidation of phosphorus. A small quantity of deposit obtained from phosphorus glowing at ordinary temperature in oxygen at 240 mm. pressure, and in presence of 98 per cent. sulphuric acid, consisted of a white, powdery substance containing a trace of yellow solid; the powder sublimed giving some minute crystals which bore a close resemblance to those obtained from the oxidation product of phosphorus trioxide. They
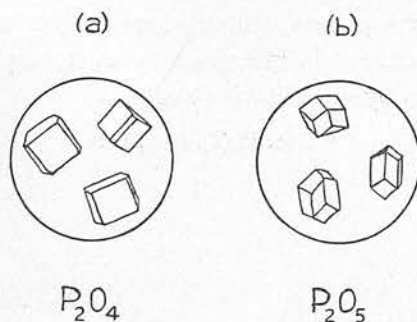
---

* Some moisture on the tube containing the solid rendered this weighing valueless.

† *Journ. Chem. Soc.*, **81**, 923, 1902.   ‡ *Loc. cit.*, p. 835.