THE SLOW OXIDATION OF PHOSPHORUS.

by

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INTRODUCTION.

It has long been known that phosphorus glows in air. In 1788 Fourcroy[1] first noticed that phosphorus when exposed to oxygen at atmospheric pressure did not glow, but that the rate of reaction increased with dilution. In 1798 Van Marum[2] found that a stick of phosphorus glowed more brightly in diluted than in ordinary air. Davy[3] found that the glow was produced in oxygen whether the pressure was reduced by admixture of nitrogen or by an air pump. Since then much work has been done on the subject and many investigators have tried to discover the reason for this seeming contradiction of the law of mass action.

PREPARATION of the MATERIALS.

Phosphorus.

Ordinary stick phosphorus was boiled in a solution of caustic soda in an atmosphere of coal gas till it was quite clear and transparent. It was then washed with water and kept under water in the dark.

A piece of this phosphorus was melted under a mixture of potassium bichromate and sulphuric acid and washed in water. This gave the same results as when treated only with soda. Solid pieces of phosphorus were sometimes used in the experiments and sometimes the phosphorus was spread on porous tile, or on filter paper or on ground glass to obtain a larger surface of exposure. This was effected by making a solution of phosphorus in carbon disulphide, putting a few drops of the solution on the surface to be prepared and blowing off the vapour of carbon disulphide by hydrogen, carbon dioxide or air. The carbon disulphide was purified by distilling with mercury and was kept over mercury. In the case of filter paper it was found to catch fire easily but the results obtained were the same in all three cases. Tile was generally used as it did not catch fire and gave a better surface than ground glass. More delicate effects could be obtained in this way than with pieces of phosphorus.

Oxygen.

The oxygen used was taken from cylinders of compressed oxygen, the oxygen content of which varied from/

from 96 - 98%, the rest being nitrogen.

ORIGIN of the GLOW.

There was some doubt in the minds of early investigators as to the origin of the glow. Two theories were suggested to explain it.

(1) That it was due to the slow oxidation of phosphorus.

(2) That it was due to the evaporation of phosphorus.

In 1797 Berthollet[4] had showed that the glow was accompanied by a slow oxidation of phosphorus but later observers stated that it glowed in pure nitrogen, in hydrogen and also in a vacuum. As further it did not glow in pure oxygen Berzelius[5] propounded the theory that it was due to the evaporation of phosphorus. Marchand[6] supported this view, but Fischer[7] showed that the glow found in nitrogen, in hydrogen and in a vacuum was due to traces of oxygen which with sufficient care could be removed - so that afterwards no glow showed. Schrötter[8] and later Joubert[9] confirmed this view and proved that the glow was due only to a slow oxidation of phosphorus.

RELATION between GLOW and OXIDATION.

It/

It being now conceded that the glow is a result of oxidation it remains to discuss whether the one is a measure of the other. It has been generally assumed that the reverse is true, viz. - that without a glow there is no oxidation. Joubert[9], Centnerszwer[10] and others consider that oxidation begins with glowing at a certain definite pressure which they term the "boundary pressure". It is doubtful, however, if this is the case. Russell[11] indeed is of the opinion that in moderately dry oxygen at high pressures there is a feeble glow which has up to this time been overlooked by other investigators, and that oxidation takes place at all pressures. He says "During the first stage of the reaction (i.e. at high pressures) there is phosphorescence but it is so feeble that it is only seen after the eye has become accustomed to darkness. In the second stage (the more rapid period) ordinary phosphorescence occurs and there is no possibility of confusing the two glows". He agrees with other investigators that oxidation begins with glowing in presence of excess of moisture at a pressure of 500 mm. Weiser and Garrison[12(b)] consider/

consider that the first step in the reaction is the oxidation of phosphorus to phosphorus trioxide which takes place without a glow and the second step oxidation of phosphorus trioxide to pentoxide which is accompanied by a glow.

It is certain that the visibility of the glow is a physiological matter depending on the length of time one has been in the dark and on the condition of the eyes before going into the dark. It is not impossible that a glow which is visible to one person may be invisible to another. A flash which is invisible if looked at directly may be seen if the eyes are fixed on a point slightly above the point at which one expects to see the flash.

When phosphorus is put into oxygen at reduced pressure it glows very brightly but this bright glow becomes gradually fainter until it disappears. Afterwards we may get intermittent luminescence, i.e. the appearance of the glow not continuously but at intervals as a flash. It has been referred to by Joubert[9], Centnerszwer[10] Rayleigh[13] and others.

<u>Experimental</u>.

<u>Experiment 1</u>.- Hydrogen from which the last traces/

traces of oxygen had been removed by passing over heated platinised asbestos, was passed over phosphorus and then bubbled through a Liebig's bulb containing a strong solution of caustic potash. After several hours the potash solution was tested for phosphate, by boiling with strong nitric acid and adding ammonium molybdate, and found to contain none.

Caustic potash does not, therefore, absorb phosphorus vapour.

Experiment 2. A similar experiment was tried with oxygen. No glow showed throughout the experiment but at the end of 5 hours the solution of caustic potash was found to contain a considerable quantity of phosphate, when it was oxidised with nitric acid and ammonium molybdate added. Some oxidation of phosphorus must therefore have taken place although no glow was visible. When air, or a mixture of oxygen and carbon dioxide, was passed over phosphorus and then through potash in the same way, a bright glow showed over the phosphorus and a much larger quantity of phosphate was obtained. So that when a glow is visible the reaction is much more rapid although some oxidation does go on in absence of a glow.

Weiser and Garrison[12(b)] /

Weiser and Garrison [12(b)] passed oxygen over phosphorus and into a heated tube. A glow showed in the tube so long as the temperature was kept above 75°. If oxygen after passing over phosphorus were passed through 10% sodium hydroxide before entering the heated tube no glow showed at all. They concluded that no phosphorus vapour is contained in oxygen passed over phosphorus - but only vapours of phosphorus trioxide. That phosphorus vapour does exist in presence of oxygen may be shown by the fact that if another Liebig's bulb containing concentrated nitric acid be added to the above experiment - after the potash bulb, at the end of the experiment the nitric acid is found to contain a considerable quantity of phosphate. This must be due to phosphorus vapour as the efficient absorption of all the oxides of phosphorus by potash was assured. If as Weiser and Garrison suggest the first step in the reaction is the oxidation of phosphorus to the trioxide without glowing and the next step the oxidation of the trioxide to the pentoxide with an accompanying glow, the first stage in the reaction must be very rapid while the second stage must be

slow/

slow.

Oxygen passing over phosphorus glowed when it met the air but no glow was obtained after it had been passed through potash. This seems to support the theory that the glow is due to the oxidation of phosphorus trioxide.

Phosphorus trioxide was prepared and it was found to give the same results with air and oxygen and gases as phosphorus. Thorpe and Tutton[18] also found this.

Experiment 3. - A piece of phosphorus was sealed in a bulb in an atmosphere of moist air and the bulb put in a thermostat at 18°. The phosphorus glowed at first but after some time the glow became fainter and finally disappeared. That this disappearance of the glow is not due to lack of oxygen is shown by the fact that on heating the bulb to a higher temperature the glow reappeared but disappeared again on cooling to 18°. The bulb was kept at 18° for three days after which time no glow showed even when the bulb was heated to 50°. It was then opened under water and approximately $1/5$ th of the volume found to have been absorbed. The action had therefore gone on till all the oxygen was used up, even although after the first day no glow was visible at 18°, the temperature at which the bulb was kept.

Experiment 4. A similar experiment was tried with a piece of phosphorus sealed in a bulb in an atmosphere of moist oxygen at a pressure of 380 mm. of mercury. As before after the first day no glow showed at 18°. but a glow was visible when the bulb was heated to 30°. Later the bulb did not glow even at 30° but glowed at 50° . After no glow showed even on heating to 50° the bulb was opened under water and only one small bubble of gas remained unabsorbed - possibly nitrogen.

Experiment 5. - A piece of phosphorus was sealed in a bulb in an atmosphere of ~~moist~~ oxygen at atmospheric pressure. The oxygen from the cylinder was bubbled through water before entering the bulb which was dry. No glow showed. After being kept for two months the action was found to have gone on to completion.

From these experiments it appears that oxidation takes place even when no glow is visible. Whether the/

the oxygen is all absorbed and only phosphorus trioxide is formed as Weiser and Garrison suggest or whether the further stage of oxidation to pentoxide may also take place without any glow, when the action is slowed sufficiently is not certain.

N.B. The glow referred to in the above experiments is the bright glow generally known, not the faint glow referred to by Russell[11].

THE REACTION.

I. Substances involved. Although it would seem at first sight that the reaction takes place on the surface of the solid phosphorus, it is now generally accepted that it takes place in the vapour phase between phosphorus vapour and gaseous oxygen. That this is the case can easily be shown by the following experiments:

Experiment 1. - A bottle was half filled with a solution of phosphorus in oleum paraffinum and corked. When the bottle was shaken the whole of the air space was lit up with a bright glow.

Experiment 2.- The end of a rod was dipped in a solution/

solution of phosphorus in oleum paraffinum, and waved in the air. The track of the end of the rod was visible for several seconds after it had passed.

Experiment 3. - A slow current of air was blown through a tube containing phosphorus. The glow showed not only over the phosphorus but all along the tube after it and even out at the end.

Experiment 4. - A stream of carbon dioxide was passed over phosphorus in a tube till no glow showed and the ends of the tube then clipped for a minute to allow the phosphorus vapour to diffuse all over the tube. A slow stream of air was then passed in and the glow showed immediately the air entered the tube, before it reached the phosphorus at all. The glow passed slowly along the tube with the air and then showed as before. By suitably arranging the rate of flow of carbon dioxide no glow was seen over the phosphorus but a glow showed at the end of the tube where the phosphorus vapour and carbon dioxide met the air. If the carbon dioxide were passed into a flask after passing over phosphorus, the flask detached after some time and air admitted - a bright glow showed all over the flask.

Experiment 5. - A stream of oxygen was passed through a tube containing phosphorus. As in the case of carbon dioxide no glow was obtained over the phosphorus but a glow was obtained at the end of the tube where the oxygen met the air. By delivering a stream of carbon dioxide at the end of the tube to dilute the oxygen further - a brighter glow was obtained.

II. Products obtained.

(a) Oxides - White oxides of phosphorus are produced during the reaction, red and yellow substances are only produced towards the end of the reaction. Russell[11] investigated the oxide produced during the first stage of the reaction. This he found to be a perfectly white substance, when heated in a vacuum a few white crystals sublimed, the rest of the substance breaking up into a white crystalline sublimate less volatile than the first, - and a red residue. The white crystalline sublimate appeared to be phosphorus trioxide and the red residue amorphous phosphorus. On treating with water the oxide only dissolved slowly. This substance he found/

found to give crystals with magnesia mixture identical with those obtained from phosphorous acid. It did not, however, melt as it ought to have done if it had been phosphorus trioxide.

Jungfleisch[14] and Weiser and Garrison[12(b)] also consider that the first product is phosphorus trioxide which is later oxidised to phosphorus pentoxide, this being the final product.

(b) <u>Ozone</u>. - Besides the main reaction in the slow oxidation of phosphorus there are side reactions. Schönbein[15] first showed that air which had passed over phosphorus was "activated" and identified the substance contained as ozone. Later investigators Corne[16], Andrews[17], Marignac and Boehe[19] confirmed this and stated that hydrogen peroxide is produced as well as ozone. Kingzett[20] and Leeds[21] were of the opinion that they were produced in a definite proportion and tried to estimate the proportions. It was difficult to separate them, however. McLeod[22] concluded that only/

only ozone and not hydrogen peroxide is present. More recently Russell[11] has shown that in absence of excess of water vapour neither ozone nor hydrogen peroxide are produced but if water vapour be present in excess both hydrogen peroxide and ozone are produced and if nitrogen also be present, traces of ammonium nitrite and nitrate. Van't Hoff[23] estimated the relative amounts of oxygen activated, to phosphorus oxidised and found that for one atomic weight of phosphorus a weight of oxygen slightly in excess of one half the atomic weight, is activated- P : $O_{0 \cdot 6}$. He ascribed the excess over the half atomic weight of oxygen to the fact that a little hypo-phosphorous acid is also formed and this as well as ozone decolorises indigo.

The reaction is usually explained by supposing that some oxygen molecules are dissociated, one atom of which goes to oxidise phosphorus while the other atom forms ozone or hydrogen peroxide. Ostwald[24] objects to this on theoretical grounds. He considers that since ozone has a higher potential than oxygen it cannot be produced directly from it, and postulates/

postulates the formation of a higher oxide of phosphorus which splits up into the lower and more stable oxide and ozone. Boehe[19], Berthelot[25], and Kingzett[20] are all of the opinion that the oxidation of phosphorus gives rise to an oxide which in contact with water generates hydrogen peroxide. Russell[11] says "If this were so it would be strong evidence in favour of Ostwald's theory and would account for all my observations, but I cannot find any evidence of such a substance".

(c). Ions. - It was found that the air which had passed over phosphorus was capable of discharging an electroscope. Among the early investigators of this are Naccari[26], Bidwell[27], and Barus[28]. There are two theories to explain this -

1. That this is due to the physical properties of the cloud.

2. That it is due to emanations in the nature of radium rays which penetrate black paper and metallic films.

Schmidt[29] considered the first theory to be the correct one, while Harms[30], Bloch[31], and Elster and Geitel[32] supported the second view. Jorissen[33] and Knoblauch[34] agree with the latter observers.

Baker[35] found that phosphorus contained in a tube which was positively charged gave a glow which had a greater effect on a photographic plate than in the case where the tube was left uncharged, and that a very slight effect was obtained on the plate if the tube containing the phosphorus were charged negatively. In a recent paper Weiser and Garrison[12(b)] have investigated this. They repeated Baker's experiment but failed to confirm his result. From their experiments they conclude that the conductivity of the air is due to ions formed during the oxidation, which act as nuclei on which oxides and water vapour condense forming a charged cloud, but that there are no rays in the nature of radium rays. They ascribe the effect on a photographic plate through black paper to the vapours of hydrogen peroxide and phosphorus trioxide which diffuse through the paper.

(d) Cloud. - The appearance of a white cloud over the surface of phosphorus at the same time as a bright glow has given rise to much discussion. Schönbein[15] considered that it was due to ammonium nitrate. This is probably incorrect. Schmidt[29] as/

as already stated, and Weiser and Garrison[12 (b)] were of the opinion that it consisted of charged particles of phosphorus oxide. It has also been suggested that it may consist of condensed water vapour.

It is certain that the cloud is only visible at the beginning of the reaction when the glow is bright. As the reaction becomes more vigorous, the glow becomes brighter and the cloud denser. In experiments with phosphorus spread on filter paper it was possible to tell by the amount of cloud whether the paper was in danger of taking fire. If the pressure were immediately increased so as to slow the reaction, the cloud disappeared and the paper did not catch fire.

RATE of the REACTION.

I. Pressure of Oxygen. If the action followed the ordinary law of mass action one might expect it to go with explosive violence at high pressures of oxygen. As has already been pointed out, this is not the case - the action at high pressures seeming to cease altogether - so that other factors must come in.

Ikeda[36]/

Ikeda[36] measured the rate of reaction in moist air and found that the rate was proportional to the pressure of oxygen. Ewan[37] confirmed this result for moist air, and claimed to have found the same for moist oxygen up to a certain pressure. In dry oxygen, however, he considered that the rate of reaction was proportional to the square root of the pressure up to 60 - 70 mm. Russell[11] repeated these results for dry and moist oxygen but does not agree with Ewan. He found that in moist oxygen the oxidation begins below 500 mm. after which it seems to follow no simple law. In dry oxygen he found that the reaction goes on at all pressures and that at high pressures, 2 to 3 atmospheres down to about 500 mm., the action is unimolecular and the rate is proportional to the pressure of oxygen. Below 500 mm. he could find no simple expression connecting the velocity of reaction and the pressure of oxygen. He suggested that the straight line found for moist air by Ewan and Ikeda might be due to the retarding influence of water vapour at one end and of nitrogen at the other, straightening out the curve at the two ends to a straight line.

Experimental.

Taking the glow as a measure of the rate of oxidation the following experiments confirmed results obtained by other experimenters. That we are entitled to make this assumption can be judged from the results obtained in the course of experimenting on phosphorus. If a glow is visible it denotes a higher rate of reaction than if no glow is visible and a bright glow denotes a higher rate than a less bright glow. For instance when phosphorus spread on filter paper is put into oxygen and the pressure reduced very slowly we get first a period of intermittent luminescence, then a continuous glow which becomes brighter and brighter as the pressure is reduced till the glow becomes a flame and the paper catches fire.

The apparatus used was as in Fig. I. The phosphorus was put in the tube (A) and oxygen blown through the apparatus. Tap (C) was closed and the pressure reduced by lowering the levelling tube (D). Mercury was used in the gauge. The 'U' tube containing the phosphorus was kept in a thermostat at/

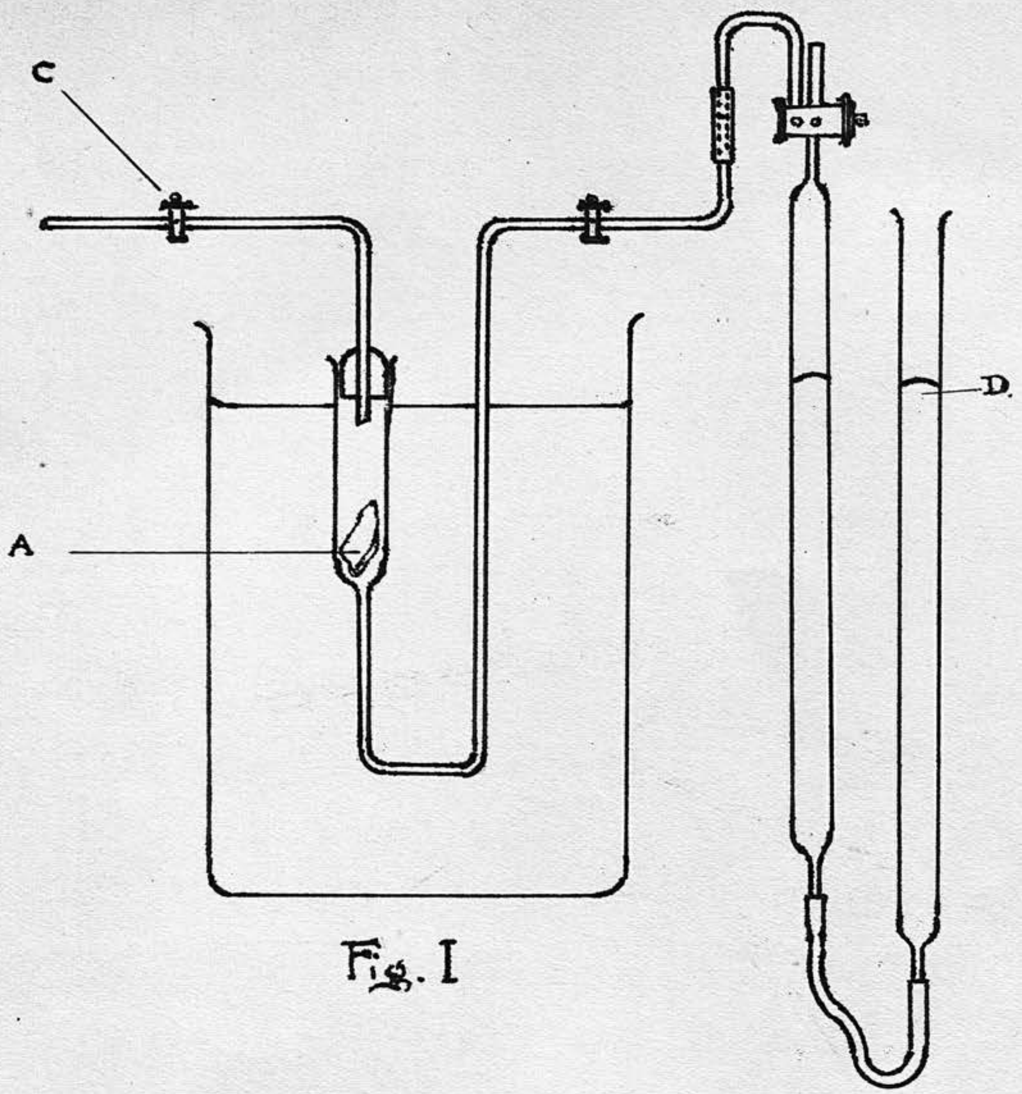

Fig. I

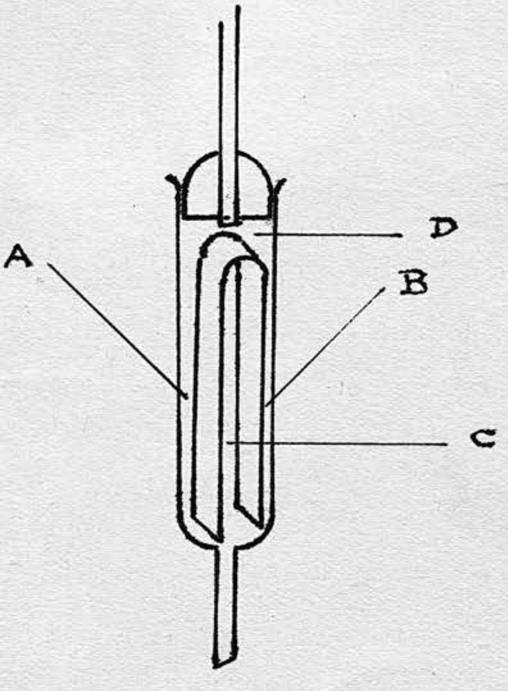

Fig. II

at constant temperature.

In moist oxygen at atmospheric pressure no glow is visible. If the pressure be lowered, at a certain point, the glow appears. If now the pressure be raised the glow disappears. The glow appears simultaneously all over the surface of the phosphorus and disappears suddenly in the same way. It does not get gradually fainter but at a certain pressure suddenly goes out. This pressure at which the glow appears - the boundary pressure - varies slightly in different experiments. If the levelling tube were lowered slowly the glow appeared at a much higher pressure than if it were lowered quickly. Centnerszwer[10] found this variation as high as 50 mm.

If the pressure were lowered to a point just above that at which the phosphorus started glowing it showed an intermittent luminescence or flash. Increase of pressure increases the interval between the flashes and decrease of pressure decreases the interval between them until at a sufficiently low pressure the flashes merge into one continuous glow. e.g. phosphorus in oxygen at a reduced pressure of

685 mm.	flashes
625 mm.	glows continuously.

II./

II. Temperature. - The actual temperature of the reaction is low. If the reaction becomes quicker the glow gets brighter and the temperature may finally be such as to set fire to filter paper. If a stream of air be passing over a piece of phosphorus at a fairly rapid rate - the edges of the phosphorus melt so that the temperature must be above 44°.

The effect of raising the temperature is to increase the rate of the reaction.

Experimental.

Experiment 1. - Two thermostats one at 18° and one at 20° were fitted up side by side in such a way that the 'U' tube containing phosphorus glowing in oxygen at reduced pressure, could be transferred from one to the other without loss of time or change of pressure. The rate of flashing increased with increase in temperature.

e.g. Phosphorus in oxygen at reduced pressure.

at 18°,	490mm.	10 flashes in 13 secs.
at 20°,	490 mm.	glows continuously with a slight pulsating effect.

Experiment 2./

Experiment 2. - In the experiments already referred to where phosphorus was sealed in a bulb in an atmosphere of oxygen at reduced pressure and kept at 18°, the glow became very faint after 5 hours and finally disappeared. When heated to 30° a bright continuous glow was visible so long as the bulb was maintained at 30°, but immediately disappeared on cooling. Later the phosphorus did not glow at 30° but glowed at 50°.

III. Pressure of phosphorus vapour.

In all the experiments above except where the temperature is changed since solid phosphorus is present one might assume that the concentration of phosphorus vapour is constant, although Ewan[37] found that by introducing Stefan's equation for the evaporation of a substance, into the equation used by Ikeda, a steadier value of K was obtained. Centnerszwer[45] by using phosphorus in solution in castor oil, petroleum and vaseline showed that as the partial pressure of phosphorus was reduced it was necessary to reduce the pressure of oxygen further before a glow was obtained.

Experimental.

In/

In order to test the effect of a varying concentration of phosphorus vapour, solutions of phosphorus were made up of different concentrations in high boiling solvents, and the temperature found at which the solution just flashed.

The solution to be tested was put into a specimen tube about 10 cms. long and 1½ cms. wide and the tube heated in a water bath the temperature of which was raised gradually, until at a certain temperature a very faint flash showed all over the surface of the liquid and immediately disappeared again. The same temperature was obtained for the flash point if the tube was heated till the phosphorus was glowing steadily and was then allowed to cool slowly - the temperature taken being the last at which a flash just showed. It was found that when air was blown on to the surface of the liquid a flash showed at a lower point than if no air were blown on to it. The temperature taken was the lowest at which a flash just showed when air was blown on to the surface of the liquid. No results were taken until the eyes had been sensitised by remaining/

remaining in darkness for half an hour. The flash was so faint that unless this precaution were taken it was not visible.

From the fact that the temperature obtained for the flash point is the same whether one approaches it from above or below, one might assume that the ozone which must be produced in the former case, has no catalytic effect - but any ozone formed is possibly blown off the surface of the liquid.

The results obtained are shown in Table I and are plotted in curves, Fig. III.

It will be seen that with falling concentration of phosphorus solution it is necessary to raise the temperature higher before a flash is obtained.

The curves for almond oil, olive oil and oleum paraffinum are coincident (A, Fig.III). Those for coconut oil, and koko butter are also coincident (B, Fig. III) and similar to the first curve but slightly higher. The curve (c) for salol is similar but higher still and that for bromonaphthalene (D) much higher than any of the others. The first three oils have practically no vapour pressure and have little effect on the reaction but koko butter/

TABLE I.

7		1		2		3		6		4		5	
Bromo-naphthalene.		Almond Oil.		Ol. Parrafin.		Olive Oil.		Salol.		Coconut Oil.		Koko Butter.	
Temp.	Conc. g.p. 100.	Temp.	Conc.	Temp.	Conc.	Temp.	Conc.	Temp.	Conc.	Temp.	Conc.	Temp.	Conc.
20.5°	.737	24°	.028	25°	.0206	24°	.0240	25°	.0848	30.5°	.0204	25°	.0288
30°	.369	25°	.0215	28°	.0154	25°	.0182	29°	.0710	33°	.0159	29°	.0197
36°	.230	30°	.0144	33°	.0103	32°	.0123	54°	.0386	42°	.0106	42°	.0101
46°	.123	45°	.0072	39°	.0078	44°	.0062	78°	.0202	73°	.0054	70°	.005
55°	.082	57°	.0056	61°	.0052	62°	.0040						
60°	.067	76°	.0037										
65°	.054												

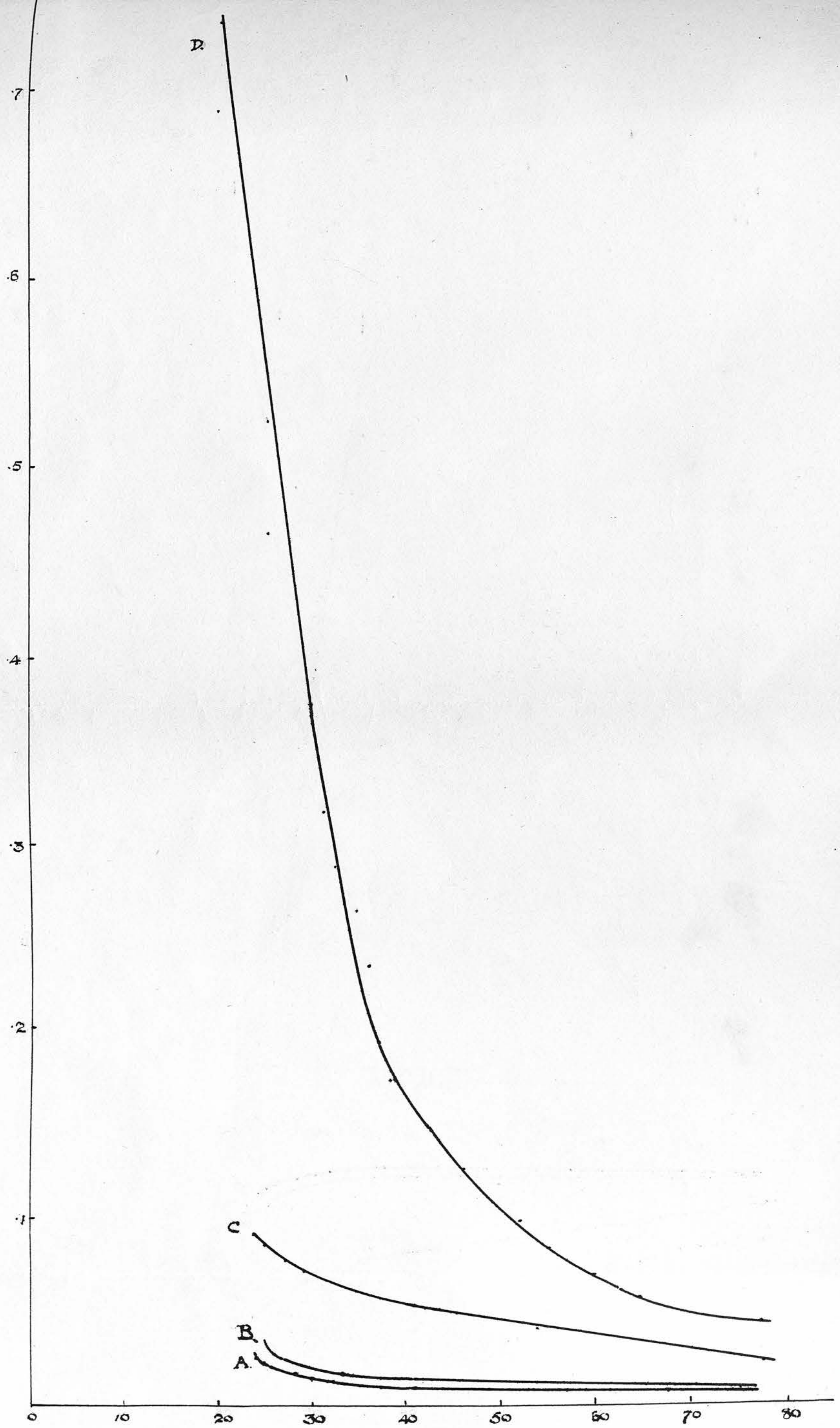

Fig. III

butter and coconut oil which have slight vapour pressures, salol and bromonaphthalene which have distinct vapour pressures act as anticatalysts and a higher temperature, resulting in a higher vapour pressure of phosphorus is necessary before a flash is produced. This is most marked in the case of bromonaphthalene.

Ewan[17] in his experiments on the rate of reaction used bromonaphthalene in some cases in his gauge and assumed it had no effect on the reaction. As each experiment was conducted at a constant temperature, however, it is possible that it only affected the actual value of K and not its constancy.

In order to estimate the pressure of phosphorus vapour which is present above the solutions at each of these flash points, the pressure of phosphorus vapour above solutions of phosphorus in Oleum Paraffinum at varying concentrations was determined. A measured volume - about 5½ litres - of hydrogen was passed through a heated tube packed with platinised asbestos to remove the last traces of oxygen, through a drying bulb, then through a Liebig's bulb/

bulb containing the solution of phosphorus to be examined, and finally through two Liebig's bulbs containing bromine water to oxidise and absorb the phosphorus vapour. The hydrogen was bubbled very slowly to ensure its being saturated with phosphorus vapour, the time taken for each 5½ litres to run through being 24 - 30 hours. The bulb containing the solution of phosphorus was kept in a thermostat at constant temperature. In the first case the temperature was 14°. The phosphate in solution in bromine water was then estimated.

Considerable difficulty was experienced in finding a suitable method for estimating the phosphate. That finally adopted was an adapted form of the method given by Raper[38] in the Biochemical Journal. The solution was boiled with strong nitric acid till all the bromine fumes were driven off and the solution boiled down to about 20 cc. The phosphate was precipitated as ammonium phospho-molybdate, washed, redissolved in ammonia and precipitated again as lead molybdate and weighed. This increases the relative weight of the precipitate to the phosphorus by more than 100 times so that although/

although the amounts of phosphorus to be estimated are very small the precipitate is quite within measurable regions. The results for each concentration were determined several times and an average taken. The maximum variation was not more than 1.0 mgm. on the weight of the precipitate which corresponds to a difference of 0.006 mgms. on the weight of phosphorus.

The vapour pressure for each concentration was calculated by the formula -

$$p = \frac{g \times 760 \times 22400 \times (273 + t^{o})}{273 \times M \times v.}$$

where p = pressure, g = weight of phosphorus,

t^{o} = temperature, M = molecular weight, v = volume.

The results obtained are given in Table II and are plotted in a curve, (Fig. IV). The results obtained for higher concentrations were vitiated by the tendency of the solution to deposit a reddish yellow precipitate of phosphorus after some time.

Table II.

Conc. Gms. per 100.	Pressure of Phosph. Vapour.		Ratio.
0.060	0.0012		50
.121	.0028		44
.242	.0036		67
.388	.0082		47
		Average	52.

The/

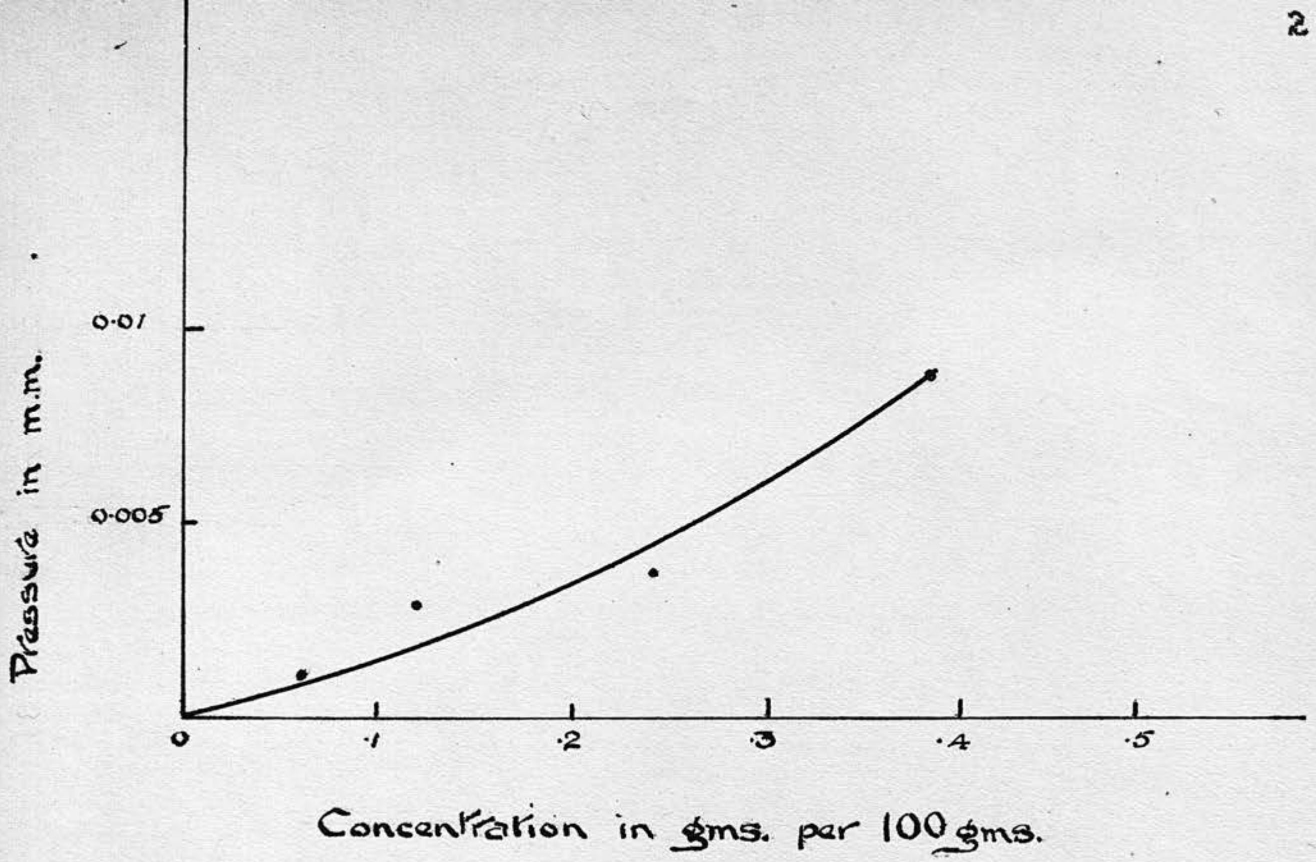
Pressure in m.m.
0·01
0·005
0
·1
·2
·3
·4
·5
Concentration in gms. per 100 gms.

Fig. IV

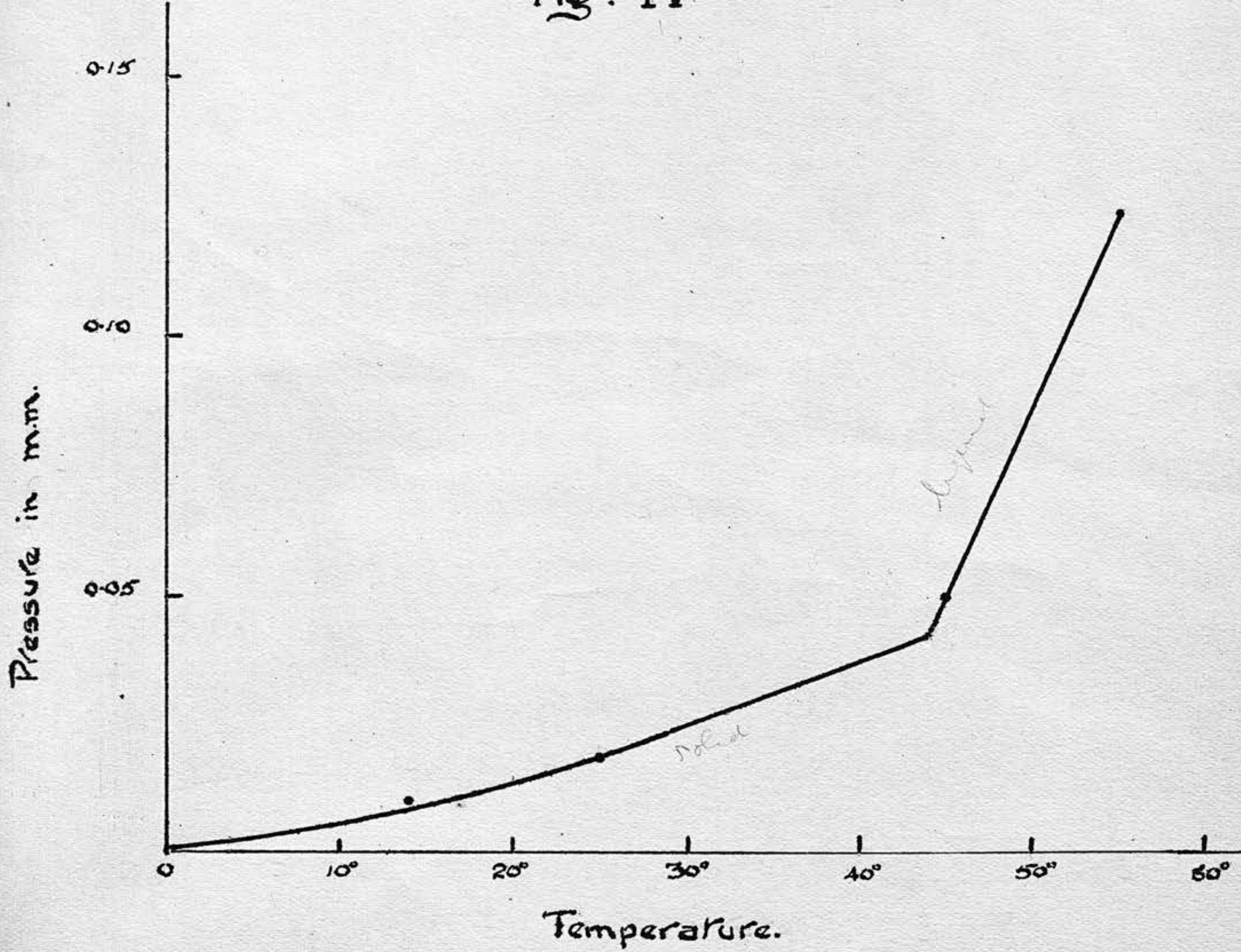
Pressure in m.m.
0·15
0·10
0·05
0
10°
20°
30°
40°
50°
60°
liquid
solid
Temperature.

Fig. V

The ratio of the concentration in solution to the pressure of phosphorus vapour above it is practically a constant, which would lead one to suppose that a distribution coefficient must exist.

An attempt was made to determine the vapour pressure of these solutions at higher temperatures but in this case owing to a distinct deposition of solid reddish-yellow phosphorus from the beginning of the experiment, the results obtained were in general lower than those obtained at 14° and were not concordant.

In order to find how the vapour pressure was affected by temperature, therefore, the vapour pressure of solid phosphorus was estimated at different temperatures. The method used was the same as for liquids but in this case, small pieces of phosphorus were packed in a 'U' tube alternately with porous tile. To ensure a larger surface of exposure a solution of phosphorus in carbon disulphide was run into the 'U' tube till the tile was thoroughly soaked. The carbon disulphide vapour was then blown off with hydrogen before the experiment started. The results obtained are given in/

in Table III and are plotted in a curve (Fig. V).

Table III.

Temperature.	Pressure.
14°	·0114 mm
25°	·0192
45°	·0508
55°	·1243

The result obtained by Centnerszwer[24] for phosphorus in hydrogen at 20° is ·0253 which is slightly higher than the result obtained by me. ~~The~~ results for phosphorus at high temperatures taken from Landolt-Börnstein are plotted along with the results given above in a curve (Fig. VI).

The solubility of phosphorus in Oleum Paraffinum was estimated. The results obtained are given in Table IV and are plotted in a curve (Fig. VII).

Table IV./

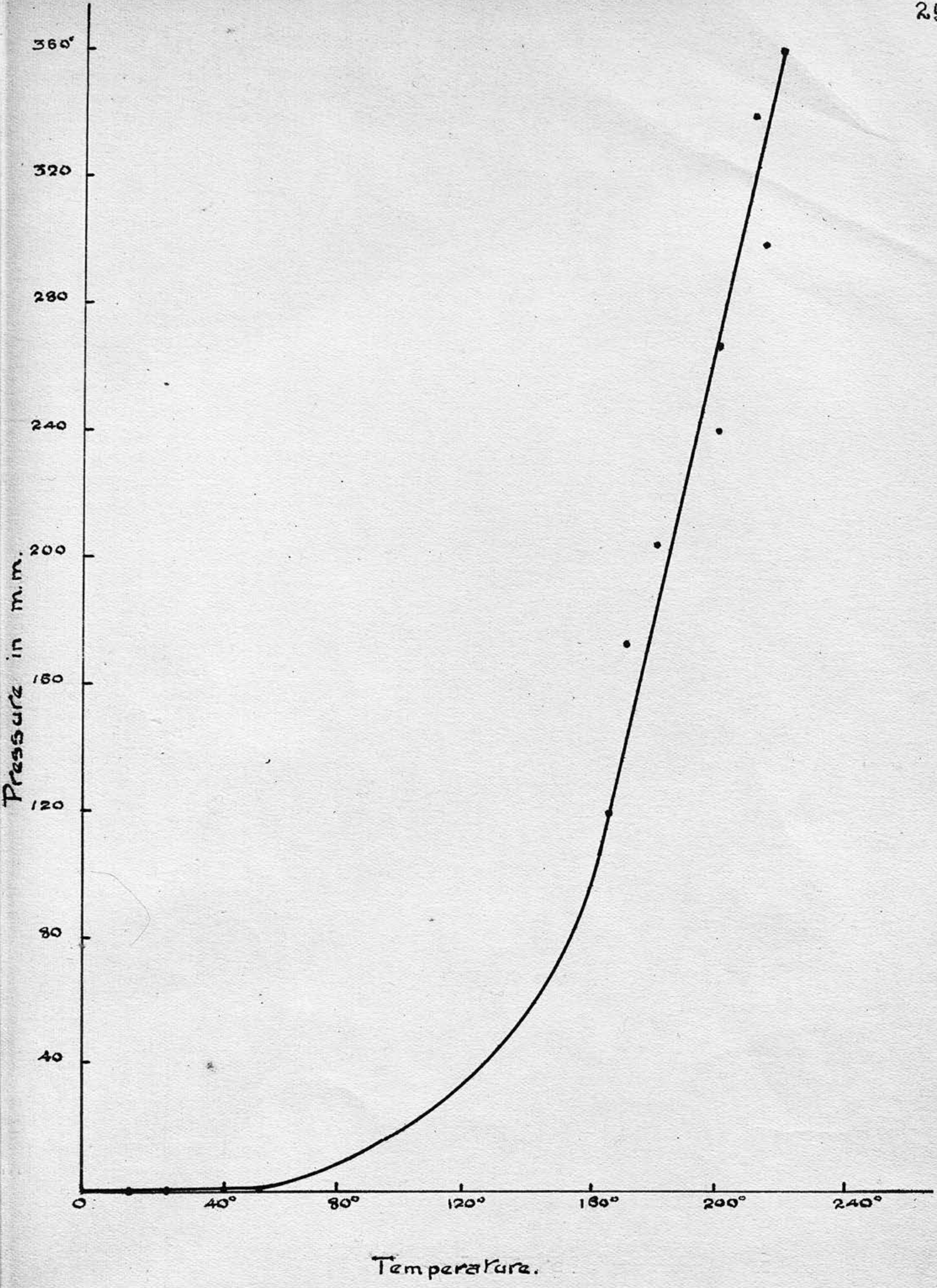
360°
320
280
240
200
160
120
80
40
0
40°
80°
120°
160°
200°
240°
Pressure in m.m.
Temperature.

Fig. VI

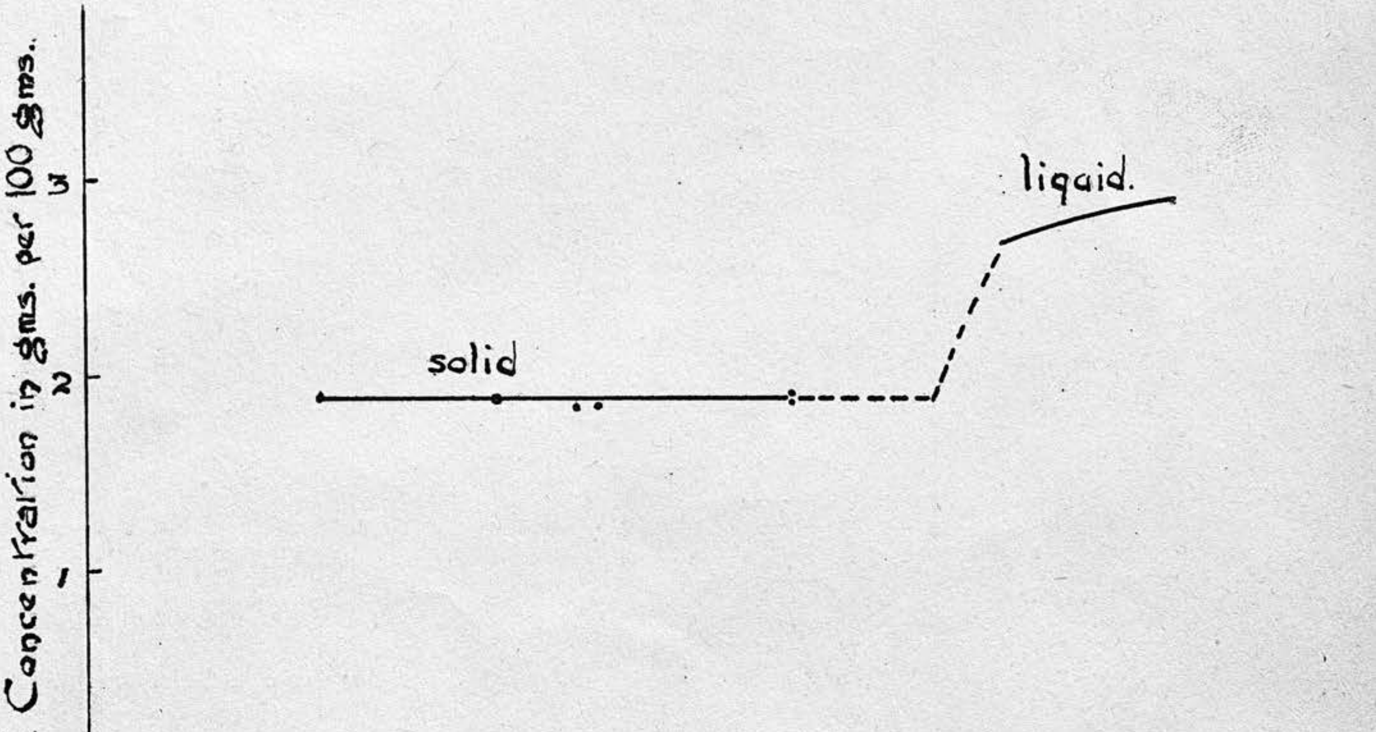
Concentration in gms. per 100 gms.
1
2
3
0
10
20
30
40
50
60
Temperature
solid
liquid.

Fig. VII

Table IV.

Conc. Gms. per 100 gms. Sat^{d}. solution.	Temperature.
1.903	12°
1.927	21°
1.900	22°
1.850	24°
1.930	36°
1.870	36°
2.700	47°
2.940	56°

Assuming that the vapour pressure of phosphorus in solution will be increased in the same ratio by an increase in temperature as the vapour pressure of solid phosphorus, from these results the values of the vapour pressure of phosphorus at the temperature and concentration at which a flash was obtained in the first three oils were calculated. The numbers are given in Table V.

Table V./

Table V.

Almond Oil.	Temperature.	Conc. gms. per 100 gms.	Press. of Phosph. Vap. x 10^{-4}.
	24°	0.0280	8.21 *
	25°	·0215	7·17
	30°	·0144	6·58
	45°	·0072	6·71
	57°	·0056	13·2
	76°	·0037	162·
Oleum Paraffinum.	25°	0.0206	6·99
	28°	·0154	5·98
	33°	·0103	5·54
	39°	·0078	5·33
	61°	·0052	16·3
Olive Oil.	24°	0·0240	7·58
	25°	·0182	6·17
	32°	·0123	6·14
	44°	·0062	5·47
	62°	·004	12·2

* The values of the vapour pressure are fairly constant up to a temperature of 45° or a little over it.

Up/

Up to a certain point the pressure of phosphorus vapour necessary to produce a flash is in all these cases a constant. Above this it is much higher. This may be due to the fact that at the higher temperatures an appreciable concentration of the vapours of almond oil, olive oil, and oleum paraffinum is present and interferes with the glow point necessitating a higher vapour pressure of phosphorus before the reaction is visible in a glow.

The vapour pressures of Bromonaphthalene at the temperatures at which a glow showed for the given concentrations, were interpolated from the figures given in Landolt-Börnstein. Assuming that the vapour pressure of Bromonaphthalene did not interfere with the pressure of phosphorus vapour, the pressure of phosphorus vapour in the solutions at the temperature necessary to produce a flash was calculated. This was divided by the vapour pressure of Bromonaphthalene at the required temperature and it was found that the value obtained was fairly constant at high temperatures.

Bromonaphthalene/

Bromonaphthalene

Temperature	K.
30°	.06
36°	.03
46°	.016
55°	·022
60°	·019
65°	·014

$$K = \frac{\text{pressure of phosph. vapour necessary to produce a flash}}{\text{pressure of Bromonaphthalene at the same temperature.}}$$

This seems to show that the hindering effect produced by Bromonaphthalene is proportional to the vapour pressure of Bromonaphthalene.

The effect of the concentration of phosphorus vapour on the appearance of a glow is further shown by these experiments.

Experiment. Phosphorus was spread on porous tile and the piece of tile left on the bench. At first it glowed brightly but after some time the glow disappeared. The piece of tile was then put into a narrow tube and it was found that the phosphorus started to flash at regular intervals.

It/

It was fastened at the closed end of a long tube the other end being left open. When the tube was inverted so that the closed end was uppermost the phosphorus flashed but not so quickly as it did if the tube were vertical and the tile at the bottom of the tube. If the stopper were **removed** from the upper end, the tile remaining suspended in the tube, no flash showed at all. If the stopper were reinserted the flashing started again.

e.g.	(1) Tile lying on bench	No flashes.
	(2) Tile in tube vertical, open end up.	10 flashes in 32 secs.
	(3) Tile in tube vertical, open end down.	10 flashes in 65 secs.
	(4) Tile in tube vertical, open at both ends.	No flash in 5 mins.
	(5) Tile in tube open at both ends, laid horizontally on bench.	10 flashes in 50 secs.

In cases (1) and (4) where free escape is allowed for the phosphorus vapour, the concentration never/

never reaches a high enough value to give a flash. Where some escape is possible as in (3) and (5) flashes appear but at longer intervals than in (2) where the vapour is more confined.

In oxygen at reduced pressure after a continuous glow had been replaced by an intermittent luminescence, if there were two sources of phosphorus with a partial separation between them, produced either by means of a constriction in the tube or by a screen of paper in the tube, these flashed quite independently of each other and the flashes did not pass across the constriction.

Experiment. A tube was roughly divided into compartments A, B, C, D, by means of a strip of filter paper bent round (Fig. II). Non-absorbent paper was gummed on the inside of the paper and across the bend on the outside. Phosphorus was spread on the two limbs of filter paper left exposed in the side compartments (A and B). These having the greatest concentration of phosphorus vapour flashed most often but did so quite independently. A flash only showed in the middle part (C) of/

of the tube if the pressure had been left at normal for a few minutes to allow the vapour to permeate throughout the tube. A very occasional flash showed in D.

IV. Catalysts.

(a) Ozone. It is generally agreed that ozone is helpful to the reaction. Centnerszwer[10] found that a trace of ozone would start the glow in oxygen at atmospheric pressure. Chappuis[39] in fact considered that in absence of ozone no action would take place at any pressure. He considered that oxygen in its usual form did not act on phosphorus at all but that the whole reaction was one of the burning of phosphorus by ozone. Jorissen and Ringer[40] attribute Russell's failure to find a boundary pressure to the fact that he took no precautions to exclude ozone.

Experimental.

Experiment. Oxygen was passed through an ozonating tube, without the current being on and then over phosphorus. After the tube had been completely cleared of air and no glow showed over the phosphorus, the current was started and after a few seconds a bright/

bright glow showed in the phosphorus.

So that ozone acts as a positive catalyst, and a small percentage is sufficient to cause a bright glow in oxygen at atmospheric pressure. That ozone is not necessary to produce a glow is shown by the fact that when oxygen before being passed into the phosphorus tube was passed through a silica tube packed with pieces of silica and heated to redness. No effect on the glow was obtained.

(b). <u>Water Vapour</u>. Baker[35] found that in complete absence of traces of moisture no action took place at all. Ewan[37] and Centnerszwer[10] also consider that a small amount of water vapour is favourable to the reaction. Russell[11] was also of this opinion, but showed that the amount of water vapour reaches a maximum after which it retards the reaction - to such an extent as to prevent its starting till the pressure is lower than 500 mm. He explains this action of water vapour by supposing that it prevents the evaporation of phosphorus by means of a physical film formed on the surface of the phosphorus.

Rayleigh[13] in a recent paper has ascribed the

intermittent/

intermittent luminescence to the retarding effect of moisture when the oxygen is nearly used up. The same intermittent effect can, however, be obtained when phosphorus is put into oxygen if the pressure be not sufficiently lowered, a lowering of pressure will produce a continuous glow, - whether excess of moisture be present or not. In his experiments with a tube, containing a layer of phosphorus, with side inlets only through capillaries he does not state whether the air entering is dry or not.

Experimental.

A piece of phosphorus was put in a tube closed at both ends by taps and provided with a side tube. The side tube was filled with water. Oxygen was blown through till no glow showed. One tap was closed and the pressure reduced to 510 mm., when the phosphorus was glowing brightly. The other tap was closed and the tube left in a bath under water at 14°. After 3 days the glow seemed at first to have disappeared but after the eyes had been further sensitised by a longer period in the dark a faint glow became visible. This faint glow remained visible for/

for a week, after which time it disappeared. The tap was opened under water and the gas was found to have been all absorbed except one small bubble - possibly nitrogen. During this time no period of intermittent flashing was seen - which would seem to show that the intermittent luminescence is not as Rayleigh[13] suggests due to the fact that water vapour acts as a negative catalyst when oxygen is nearly used up.

A similar experiment was tried with the tube dried and air moderately dried. In this case the glow showed as before getting gradually fainter but the reaction finished in a much shorter time than when a large excess of water vapour was present.

(c). Other Gases and Vapours.

Graham[41] found that some gases when added to phosphorus glowing in air immediately stopped the glow, while other increased it. He found that at 25° one volume of Ethylene in 450 volumes of air was sufficient to stop the glow, one volume of ether in 150 of air and 1 of turpentine in 1440 of air. To bring back the glow it was necessary to raise the temperature or reduce the pressure. Davy[3] confirmed/

confirmed and extended Graham's results. Later Centnerszwer[10] investigated this aspect of the subject. He made up mixtures of oxygen with a known concentration of the gas and introduced phosphorus into them. The pressure was slowly reduced by an air pump, and the point at which the glow became visible noted. Several concentrations for each gas were examined in this way and the results plotted on curves. From these he calculated A, the lowering of the boundary pressure for each percent of the catalyst; and B, the curvature of the curve. He deduced that in presence of the saturated vapour of all homologues the glow pressure remains in approximately the same region. Isomers he found to have the same effect. In a later paper[44] he showed that this retarding effect is not due to the fact that these gases prevent the evaporation of phosphorus. He estimated the vapour pressure of phosphorus in presence of hydrogen, oxygen, carbon dioxide, illuminating gas and in air and iodobenzene and found that there was little difference between/

between the results obtained.

Jorissen[33] has shown that in presence of those gases which act as poisons the effect on a photographic plate covered with black paper is not obtained.

Weiser and Garrison[12(c)] consider that during the oxidation of phosphorus, ions are formed which consist of oxide particles about charged nuclei. "Vapours are adsorbed both on the charged and uncharged particles. Those gases which react with phosphorus trioxide increase the velocity of the reaction by removing oxide particles from the zone of reaction and by raising the temperature. If the vapours are inert they prevent further oxidation of phosphorus trioxide and also form a cloud near the surface of phosphorus which slows down the action. This cloud approaches nearer and nearer the surface as the oxidation becomes less and less energetic and may form a protecting film which reduces vaporisation and oxidation of phosphorus to a minimum." That all those gases which act as promoters of the glow such as nitrogen do not react with phosphorus trioxide is obvious on considering the list of diluents and poisons given below.

Experimental./

Experimental.

The slowing effect which the presence of the vapours of Bromonaphthalene and salol and to a much lesser degree koko butter and coconut oil exerts on the reaction has already been shown. That this poisonous effect is not permanent can be shown by the fact that as soon as the gas is shut off and only air, or air and oxygen are present above the phosphorus the glow comes back. In order to see whether any common property could be found which belonged to the gases which decrease the glow - the effect of a number of gases and vapours - organic and inorganic - was tried.

An apparatus was arranged so that a stream of a mixture of air and oxygen in varying proportions could be obtained, and passed through a tube containing phosphorus. A third entrance was arranged so that another gas could be passed into the mixture and the whole then passed through the tube containing phosphorus. Each entrance was provided with a stopcock and a screw clip so that the flow of gas could be regulated or shut off. The stream of air and oxygen was/

was first arranged in such a way that a glow in the phosphorus could just be seen. A slight increase in the flow of oxygen or a decrease in the flow of air immediately ~~put it out~~. The third entrance was then opened and a small amount of the gas to be examined allowed to enter, the effect on the glow being noted. It was found in accordance with other experimenters that some gases increased it and some put it out. Those which increased it have been classed as diluents and those which put it out as poisons. By suitable arrangement of the currents of air and oxygen giving a brighter or more feeble glow, and of the amount of gas which it required to put it out it was possible to classify the poisons as relatively strong and weak. Those gases which acted as the strongest poisons are classed as P_1, weaker poisons as P_2 and so on.

If the substance under examination were a liquid with a high vapour tension and not a gas, the route of the air was changed to pass through it, care being taken that the actual flow of air was unchanged in the process.

The/

The results are tabulated below.

P_1.	P_2.	P_3	P_4	P_5	Diluents.
Carbon disulphide.	Acetylene.	10% Ethyl alcohol.	Sulphur dioxide.	Aniline.	Hydrogen.
Ethylene.	Ethane.	1% acetone.	Glowing phosphorus.	Acetic acid.	Carbon monoxide.
Nitric Oxide.	Pentane.	Benzaldehyde.		Phenol.	Methane.
	100% Ethyl Alcohol.	Formaldehyde.			Nitrogen.
	Benzene				Carbon dioxide.
	100% acetone.				Phosgene.
	Paraldehyde at 33°.				

The effect of aniline, acetic acid and phenol is barely perceptible. The case of ammonia and methyl alcohol may be mentioned specially. They have a very slight tendency to increase the glow. They will not start it as is the case with the other diluents but if a feeble glow is showing they tend to make it brighter. Rayleigh[13] classes ammonia as a poison/

poison and compares it with water vapour.

This peculiar effect of gases and vapours some acting as poisons and others as diluents or promoters of the glow, has been explained by Schönbein and Chappuis[39] as a result following on the property possessed by the poisons of destroying ozone. Chappuis, as already stated, considered that in complete absence of traces of ozone no action would take place. Centnerszwer was doubtful of this and stated that although in some cases the parallelism held the evidence was not sufficient to enable one to come to a definite decision. Weiser and Garrison state that Centnerszwer considers that turpentine is not an ozone destroyer - but he says "turpentine seems to have the strongest effect on the glow of phosphorus, while its ability to absorb ozone is well known".

Experimental.

The effects of some of these gases was tried on ozone, and the following classification made.

Ozone destroyer.	Non destroyer.
Ethylene	Hydrogen.
Benzene	Methane.
Ethyl Alcohol } (weak destroyer).	Ethane.
	Pentane.

Ethylene and benzene are both strong poisons and strong ozone destroyers which would seem to support Chappuis' theory. Alcohol, however, is also one of the strong poisons but has a slight effect on ozone. Hydrogen and methane are both promoters of the glow and are non destroyers of ozone which would seem to support the theory, but ethane and pentane which are strong poisons have no effect on ozone. It may be noted that methane, ethane and pentane are all saturated hydrocarbons and have no effect on ozone which is what we should expect, but the fact that the first member of the series, methane should be a diluent while the others are poisons is difficult to explain. Methane must possess some property which the others have not or must lack some property which the others have. That the poisonous effect can not be due to the property of destroying ozone is evident.

In a paper on the effect of positive rays on gases and vapours J. J. Thomson[42] says he has found only two cases where a molecule of an element acquires a negative charge - oxygen and carbon.

The/

The conditions for the appearance of the negatively charged oxygen molecule he has not worked out, but he says "The conditions which regulate the appearance of the negatively charged carbon molecule have been worked out and are very interesting. The negative molecule does not occur in compounds like marsh gas, carbon dioxide, carbon monoxide, phosgene etc., where there is no linking between carbon atoms. On the other hand it does occur with compounds like acetylene, ethylene, ethane, where there are two carbon atoms linked together by one or more bonds".

This is interesting from our present point of view as all those gases which Thomson says are capable of developing negatively charged carbon molecules are poisons - the others which do not give negatively charged carbon molecules are promoters of the glow. No other property common to marsh gas, carbon dioxide etc., and not possessed by the other members of the saturated hydrocarbon series - ethane, pentane, etc., has been found. Methyl alcohol which has only a single carbon bond and should not give negatively charged carbon molecules is not a poison. The case of/

of chloroform is peculiar - it seems to put out the glow at first but later the glow reappears. The case of carbon ~~dioxide~~ disulphide however is not explained by this - although it may be that it gives negatively charged molecules. More gases would have to be tried under the positive rays before a definite conclusion could be arrived at. The case of nitric oxide is difficult to explain but it may be that it gives negatively charged oxygen molecules.

(d) Radium Bromide.

Jorissen[33] found that Radium bromide had no effect on the glow.

Experimental.

A mixture of air and oxygen was passed through a tube, with a piece of phosphorus at one end, in such a proportion as just to put out the glow. A small tube containing 1 mgm. of radium bromide was wrapped in black paper and passed along under the tube. A very faint glow showed in the tube above it, as it passed along. That this was not due to phosphorescence in the glass or to any peculiar quality of the syrupy phosphoric acid, present in the tube as a result of the/

the reaction, was shown by the fact that if the piece of phosphorus were taken out and the tube otherwise left as before, no glow now showed on passing the radium bromide along. This glow was very faint and could only be seen after the eyes had been sufficiently sensitised, and when great care was taken. If oxygen alone were passing over phosphorus radium bromide did not produce a glow.

(e). Other Effects.

Several investigators have referred to the slowing of the reaction with time. This ~~is not~~ because it is nearing the end of the reaction and does not depend on a lack of oxygen, nor if one would judge from the presence of solid phosphorus in the tube, from lack of phosphorus vapour. Müller[43] found that phosphorus which had been standing in diluted oxygen for 43 hours no longer glowed, nor did the glow reappear on further dilution. He concluded that during oxidation something is produced which acts as a deterrent and stops the reaction. Van't Hoff[23] also refers to this hindering effect and found it could be removed by shaking with indigo sulphonic acid.

Experimental./

Experimental.

I. Experiment. Phosphorus was put in oxygen (Fig.I) and the pressure reduced till a bright glow showed. After a short time without appreciable change of pressure the phosphorus ceased to glow continuously and glowed only in flashes. The time between the flashes was marked by a stop watch and it was found that the flashes appeared at quite regular intervals, but these intervals gradually became longer and longer until no glow showed at all. e.g. Phosphorus in moist oxygen - pressure 380 mm. (adjusted throughout the experiment but required little adjusting), Temperature 18°.

Time.	Glow.
0	Glowing continuously.
6 mins.	10 pulsations in 14 secs.
14 mins.	10 flashes in 18 secs.
22 mins.	10 flashes in 27 secs.
1 hour.	1 flash in 32 secs.
1 hour 10 mins.	1 flash in 35 secs.
2 hrs. 35 mins.	1 flash in 2 mins.
18 hours.	No flash in 10 mins.

Experiment 2. - After the flashes had become

slower/

slower if the levelling tube were raised and lowered so as to mix the gas in the burette above the phosphorus - the glow might become continuous if the time which had elapsed were not too long.

e.g. Phosphorus in oxygen, pressure 380 mm. temp. 18°.

Time.	Glow.
0	Glowing.
10 mins.	10 pulses in 15 secs.
12 mins.	10 pulses in 30 secs.
15 mins.	10 flashes in 3 mins.
Gas in tube mixed.	10 pulses in 25 secs.

Experiment 3.- It was found that by lowering the pressure after the flashing had stopped, the glow could be reproduced, but as time went on a lower and lower pressure was required to produce it.

e.g. Phosphorus in oxygen, temperature 18°.

Time.	Pressure.	Glow.
0	372	Glowing.
24 hours.	372	No flash in 30 mins.
	322	do do do
	272	2 flashes interval 7 mins.
	372	No flash in 30 mins.
	272	2 flashes interval 6 mins.

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Experiment 4. - After the phosphorus has ceased to glow on a further reduction of pressure, It was found that if fresh oxygen were blown through the tube - the tube being otherwise left exactly as before, the glow reappeared ~~again~~.

~~e.g.~~ Phosphorus in Oxygen, temperature 18°.

Time.	Pressure.	Glow.
0	360 mm.	Glowing.
18 hours.	360 mm.	No flash in 10 mins.
Fresh oxygen blown through.		
	360 mm.	Glowing continuously.

The same slowing effect with time is shown in the experiments given above where phosphorus was sealed in a bulb. The glow which was visible at 18° at first, required later to be heated to 30° before a glow appeared. All these results could be obtained with phosphorus in solution in Oleum Paraffinum; Centnerszwer[45] found a similar result.

SUMMARY and DISCUSSION of RESULTS.

Oxidation of phosphorus may take place without visible glow. (pps. 8 - 9).

For a glow to be visible the action must occur at a certain rate below which no glow appears.

The action which produces the glow is probably the oxidation of phosphorus trioxide. This action must take place at a considerably less rate than the oxidation of phosphorus to phosphorus trioxide which precedes it. (pps. 6 - 7).

The glow occurs chiefly in the gas phase and may be steady, fluctuating or intermittent (pps. 10 - 11). The intermittence or fluctuation is explicable by the slow accumulation of oxidisable vapour and subsequent oxidation with glow, for which a certain pressure of oxidisable vapour derived from phosphorus is necessary (pps. 22 - 36).

The rate of the reaction is increased with rise of temperature, (p. 21).

At partial pressures of oxygen near one atmosphere the rate is diminished with rise of oxygen pressure, and may be slowed below the glowing point, (19 - 20).

Certain/

Certain gases act as positive catalysts and others as negative catalysts or poisons, (pps.42-44).

The presence of ozone in oxygen greatly increases the glow, but the glow itself is not under ordinary conditions due to ozone produced in the reaction.(pps.36-37). A trace of moisture seems necessary to start the reaction, but as the pressure of water vapour increases the rate reaches a maximum and thereafter falls, (pps. 37 - 39).

The reaction as time goes on seems to be automatically slowed below the rate at which a glow is visible. This slowing may be overcome by raising the temperature, or by reducing the pressure of oxygen or by a gradual accumulation of the vapour (pps49-52).

The retarding effect which certain vapours have on the reaction is not due to their ozone destroying properties (p. 45), nor to the fact that they prevent the evaporation of phosphorus (Centnerszwer).

The fact that the reaction is slowed in oxygen near atmospheric pressure and automatically slows itself in oxygen at lower pressures is attributed by Weiser and Garrison[12(a)] to the fact that a film of oxide/

oxide forms on the surface of the phosphorus and prevents its evaporation. They consider that when the concentration of oxygen is high the reaction takes place more quickly than the phosphorus can evaporate and is thus forced down on to the surface of the phosphorus forming a protective film of oxide. When the pressure is lowered this film is broken. The fact that the glow can be blown off the surface of the phosphorus by a rapid stream of air they ascribe to the same reason, the concentration of oxygen being high in this case also. Intermittent luminescence they consider is caused by the make and break of this film.

Russell is of the opinion that the slowing of the reaction in presence of moisture so that no glow shows till the pressure is lowered below 500 mm. is due to a protective physical film formed by the water vapour.

That the effects obtained can be due to the formation of a protective film whether physical or chemical is unlikely as exactly the same effects are obtained/

obtained with phosphorus in solution in olive oil, oleum paraffinum etc. That a film could protect the phosphorus in this case is most improbable as shaking the solution does not reproduce the glow.

Several experimenters are of the opinion that this slowing effect is due to a negative catalyst produced during the reaction. The fact that phosphorus which under a reduced pressure of oxygen has ceased to glow, will glow brightly again if fresh oxygen be blown into the tube, supports the theory that the retarding effect is due to an anticatalyst and not to a film. The fact that air which has passed over glowing phosphorus acts as a weak poison in spite of the fact that it must contain some ozone which is helpful also supports the theory of the production of an anticatalyst, whose poison effect is greater than the helpful effect of ozone. A similar conclusion may be deduced from the fact in a dilute solution of phosphorus in oleum paraffinum the glow was visible at a lower temperature, when fresh air was blown on to the surface of the liquid, (p. 23).

Van't Hoff considers that this hindering effect is/

is due to positive and negative ions which are produced during the reaction.

From the results obtained and in consideration of J. J. Thomson's results it seems most probable that this negative catalyst consists of negatively charged molecules. It has been pointed out (p. 47) that those gases which act as poisons are those which are capable of developing negatively charged carbon molecules. Although the conditions of the appearance of negatively charged oxygen molecules have not been worked out, it may be that at high pressures of oxygen these negative molecules are so abundant as to prevent the glow from showing. At lower pressures of oxygen they are possibly present in smaller quantity and the glow shows at first, but as the action goes on they are produced in sufficient quantity to slow the action below the glowing point. If the concentration of phosphorus vapour be increased this slowing effect can to a certain extent be overcome. That it is possible to do so has been shown (p. 25). For this reason an increase in temperature ensuring a higher concentration/

concentration of phosphorus vapour will reproduce it. A decrease in pressure followed by a more rapid evaporation of phosphorus may ensure that the concentration of oxidisable vapour necessary to produce a glow be reached. As time goes on this concentration will only be reached at longer and longer intervals.

That gases which do not develop negatively charged molecules act as diluents and promote the glow is possibly due to the fact that they reduce the concentration of negative molecules without affecting the concentration of phosphorus vapour.

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