CXX.—The Reaction between Phosphorus and Oxygen. Part I.

By EDWARD JOHN RUSSELL.

It is well known that the rate of oxidation of phosphorus increases as the pressure of oxygen diminishes, and no satisfactory explanation of this apparent exception to the law of mass action has yet been given. A careful study of the reaction has been made, and several other anomalies have been found. This paper contains the results of the first part of the investigation.

Preparation of the Materials.

(1) The phosphorus, which had been proved to be free from arsenic, was heated with phosphorus trichloride in a sealed tube at 200° for two days in order to decompose any hydride; the trichloride was then distilled off, the last traces being removed in a current of carbon dioxide. Another tube, with side tubes attached, was now sealed on to the reaction tube and the apparatus exhausted. Heat was applied, when the phosphorus distilled over and was collected in the side tubes, the pump being continuously in action so as to remove the small quantities of gas which are evolved. The tubes, which were quickly sealed off and kept in a dark place, now contained the phosphorus as a clear, highly refractive liquid, which after a time set to a white, waxy solid.

(2) The method of purifying the phosphoric oxide was that recommended by Shenstone and Beck (Trans., 1893, 63, 475), the oxide being distilled in a stream of oxygen over red-hot spongy platinum until the product no longer reduced a solution of silver nitrate.

(3) The oxygen was obtained from recrystallised potassium chlorate which had been kept fused for some time to expel moisture. This was

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transferred to a hard glass tube closed at one end, and the other end was then drawn out to form a delivery tube.

Duplicate experiments were sometimes made with oxygen obtained from potassium permanganate, but no difference in the results could be detected.

The apparatus (see Fig. 1) was thoroughly cleaned out with boiling concentrated nitric acid and dried at a high temperature. The end of the gauge C was dipped under mercury, and the whole exhausted by a Töppler pump. Purified phosphorus pentoxide was then distilled into B and D and phosphorus into A, the pump being meanwhile kept working. The supply tubes containing these two reagents were then



sealed off, and the apparatus left as shown in the sketch. After some months, when it was thought that drying was complete, the second part of the apparatus was sealed on through a T-piece afterwards joined to the pump. This was so arranged that the oxygen generated in G could, in the first series of experiments, pass through the phosphorus pentoxide in E, and in the second series through the sulphuric acid in F before reaching the phosphorus. The completed apparatus was exhausted, and left standing for a further period.

First Series.—A and B were surrounded by a bath of ice and salt, and oxygen introduced until the pressure was about 50 mm.; the temperature was raised to 15° , and the time required for absorption

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was found to be about one hour. The amount of water present in oxygen, when dried in this way, is considered by Morley to be not more than 1 milligram in 40,000 litres (*Amer. J. Sci.*, 1887, 34, 200).

Second Series.—The oxygen, being dried by sulphuric acid, contains about 1 milligram in 400 litres (Morley, *loc. cit.*); the rate of absorption was very rapid, only 2 or 3 minutes being required.

Third Series.—Two similar tubes containing quantities of phosphorus with approximately equal surfaces were prepared (see Fig. 2) and filled with oxygen. In the one, sulphuric acid was present, and in the other, water. The dried phosphorus reacted much more quickly than the moist.

These experiments show that an increase in the amount of water increases the velocity of oxidation, but that a maximum is soon reached, after which further additions have a retarding influence. Many attempts were made to determine the limits within which the most favourable quantity of water lay, but with only partial success. The general result was that oxidation was most rapid when the phosphorus and oxygen had been dried over sulphuric acid, and the phenomena of oxidation in these circumstances were carefully observed.

Substances formed during Oxidation.

Schönbein (Poggendorff's Annalen, 1845, 65, 69; also *ibid.*, 169) and Schmidt (J. pr. Chem., 1866, 98, 414) showed that unless water is present neither hydrogen peroxide nor ozone is produced. My experiments fully confirm this result. Phosphorus was distilled into an exhausted tube connected at either end with sulphuric acid drying bulbs; the apparatus was left to dry; oxygen was passed through and then treated with potassium iodide and starch solution. The experiment was repeated under pressures varying from 100 mm. to 760 mm., both with oxygen and air, but, although oxidation was rapid and the phosphorus glowed brightly, ozone could not be detected.

When moist oxygen was passed over the phosphorus, both ozone and hydrogen peroxide were formed in notable quantities.

The production of ozone during the oxidation of phosphorus, therefore, requires the intervention of a large amount of water, and does not take place in presence of the small quantity most favourable for the reaction of oxidation. The experiments dealt with in this part of the paper are therefore not complicated by the presence of ozone or hydrogen peroxide.

The oxides produced are white ; red and yellow substances are only produced in the light or towards the end of the reaction when, as will afterwards be seen, the velocity of oxidation increases rapidly and the temperature rises.

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The Velocity of Oxidation.

Ikeda (Journ. Coll. Sci. Imperial Univ. Japan, 1893, 6, 43) has studied the velocity of oxidation in moist air and found that it was proportional to the partial pressure of oxygen up to a certain point. Ewan, in a very interesting paper (Phil. Mag., 1894, 38, 505), confirmed this result, and claimed to obtain a similar one for moist oxygen. In dry oxygen, however, the process appeared to be different; the velocity seemed to be proportional to the square root of the pressure He supposed that the rate of oxidation was proportional of the gas. also to the rate of evaporation of the phosphorus, and modified the usual equation by introducing Stefan's equation, $v = c \cdot \log P / (P - p')$, where v, P, p' are the rate of evaporation, total pressure, and vapour pressure of the evaporating substance respectively, whilst c is a This expression was obtained by studying the rate at which constant. ether evaporated in a tube, the end of which was open to the air. The equation therefore becomes :

$$-dp/dt = Kp \cdot \log P/(P - p'),$$

where p is the partial pressure of oxygen, P the total pressure due to oxygen, nitrogen, water vapour, and phosphorus vapour, and p' the partial pressure of the phosphorus vapour. This is easily integrated and gives :

$$Kt = \frac{P_0 - P}{p'} - \left(\log \frac{P_0 - a}{P - a}\right) \left(\frac{a}{p'} - \frac{1}{2}\right),$$

where P_0 is the total pressure at the beginning of the reaction, and a the pressure of nitrogen, water, and phosphorus.

As indicated by Ewan's tables, the values of K appear to be fairly constant in the experiments with moist air, but this does not usually happen with moist oxygen; out of nine experiments, satisfactory results were obtained only in three cases. It cannot either be said that the results justify the expression given for oxidation in dry oxygen; the total fall of pressure was 200 mm., but only over the last 70 mm. do the results agree with the expression.

In Fig. 2 (p. 1267), C is a tube containing glass wool soaked in pure sulphuric acid, the excess of which can run to the bottom at g. Into this is sealed a wide tube, B, carrying some bulbs and also a wide tube, A, to hold the phosphorus. D is a mercury gauge, G is connected with a Töppler pump, and F with a Jena glass tube containing the potassium chlorate.

The apparatus having been exhausted, A is heated and pure phosphorus carefully distilled into B, the pump being again continually in action so as to remove the last traces of gas; finally A is sealed off. The phosphorus collects in large drops all over B, a layer of liquid also lies in the bulbs. A large surface is essential to the success of the experiment. A tin bath is now placed round B and C, filled with a mixture of ice and salt, oxygen is generated, at first to wash out the apparatus and then to fill it under atmospheric pressure, the apparatus is then sealed off at E, being thus disconnected from the pump and the oxygen generator, finally the freezing mixture is displaced by water at a constant temperature. After two or three hours, readings of the pressure were taken by means of a cathetometer and a standard brass scale. The results are set out below in the first two columns; the numbers given in the columns K_1 , K_2 , &c., are obtained by substituting





the experimental values in the four equations given below. Should any one of the equations represent the progress of the reaction, the numbers obtained would be constant.

Under the heading K_1 are given the values calculated from the ordinary equation,

$$-dp/dt = K_1 p_2$$

which, on integration, gives

The values of K_2 are calculated from the equation

$$-dp/dt = K_2 p^{\frac{1}{2}};$$

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on integration, this becomes

the rate of oxidation being supposed to be proportional to the square root of the pressure of oxygen, in accordance with Ewan's deduction.

For K_3 , the equation

$$-dp/dt = K_3 p \log P/(P - p')$$
 (3)

was used, and for K_4 the equation

$$-dp/dt = K_4 p^2 \log P/(P-p')$$
. (4).

Equations (3) and (4) are derived from equations (1) and (2) by assuming that the rate of oxidation is also proportional to the rate of evaporation. The integration of (3) leads to the result:

$$K_{3}t = \frac{P_{0}-P}{p'} - \left(\log \frac{P_{0}-a}{P-a}\right) \left(\frac{a}{p'} - \frac{1}{2}\right).$$

Now a = p', and p' is very small compared with P, hence the first term $(P_0 - P)/p'$ becomes so great compared with the second term $\frac{1}{2}\log(P_0 - a)/(P - a)$ that this can be neglected, whereupon the equation becomes

p' being constant.

The integration of equation (4) gives the result

$$K_{4}t = \frac{2}{3p'}\left[\left(P_{0}-a\right)^{\frac{3}{2}}-\left(P-a\right)^{\frac{3}{2}}\right] + \left(\frac{2a}{p'}-1\right)\left[\left(P_{0}-a\right)^{\frac{1}{2}}-\left(P-a\right)^{\frac{1}{2}}\right]$$

and since a = p' and $(P_{0^{\frac{1}{2}}} - P^{\frac{1}{2}})$ is small compared with $(P_{0^{\frac{3}{2}}} - P^{\frac{1}{2}})$, this becomes

By differentiating (5) we get

$$dp/dt = K',$$

and by differentiating (6) we get

$$dp/dt = K'' p^{\frac{1}{2}},$$

or, in other words, the assumption that the velocity of reaction is proportional both to the pressure of oxygen and to the rate of evaporation of the phosphorus leads to the same result as the assumption that the velocity is altogether independent of the pressure of oxygen; whilst the hypothesis that the rate of oxidation is proportional both to the square root of the partial pressure of oxygen and to the rate of evaporation of the phosphorus leads to the same result as the assumption that the velocity is inversely proportional to the square root of the partial pressure of oxygen.

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It should be noted that the values K_1 , K_2 , &c., are not the absolute values, but only proportional to them. To obtain absolute values, a knowledge of the active mass of the phosphorus would be required, a determination which would be difficult, if not impossible, to carry out, and which seems to be unnecessary, for so long as the surface is sufficiently great the active mass can be assumed to be constant in any given experiment, although the values of K, &c., obtained in different experiments cannot be compared.

Time in hours.	Pressure of oxygen in mm.	<i>K</i> ₁ .	K ₂ .	K ₃ .	K4.
0	669.82		_		
0.75	638 24	279	82.4	421	162
3.00	527.49	346	97.1	474	174
3.20	497 99	368	102	490	178
4.00	468.20	389	106	504	180
5.08	395.12	451	118	540	187
6.25	295.35	569	139	599	196
6.75	236.05	671	156	642	203
7.00	200 42	749	167	671	207
7.25	163.14	846	181	699	210
7.53	106.87	1058	206	747	215
8.08	nil	1068	3 35	866	224

Expt. 1. $t = 18.6^{\circ}$.

(See Curve 1, p. 1270.)

Expt. 2. $t = 13.8^{\circ}$.

Time in hours.	Pressure of oxygen in mm.	<i>K</i> ₁ .	K ₂ .	K ₃ .	K4.
0 3.00 4.75 5.75 6.75 7.75 8.00 8.25 18.5 20	342·54 323·74 308·94 298·18 287·55 277·35 274·14 272·01 80·66 nil	816 944 1047 1126 1183 1209 1214 3395 —	172 196 215 230 239 244 244 515 925	92 103 113 119 126 125 125 211 281	167 187 202 212 217 220 220 220 301 322

In each case, the absorption began at 770 mm. pressure, but the earlier readings were not taken.

Experiments tried at a higher temperature (25°) failed because the

phosphorus caught fire when the pressure had fallen to about 500 mm.

Experiments were next made in which calcium chloride replaced sulphuric acid as the drying agent.



CURVE 1.

Expt. 3. $t = 16.6^{\circ}$.

Time in hours.	Pressure of oxygen in mm.	<i>K</i> ₁ .	K ₂ .	K3.	K4.
$\begin{array}{c} 0 \\ 1 \cdot 00 \\ 2 \cdot 00 \\ 3 \cdot 50 \\ 4 \cdot 00 \\ 4 \cdot 50 \\ 5 \cdot 50 \\ 6 \cdot 30 \\ 6 \cdot 50 \\ 6 \cdot 75 \\ 7 \cdot 00 \\ 7 \cdot 15 \\ 7 \cdot 20 \end{array}$	534.55 486.00 486.73 358.87 332.52 303.80 272.82 238.59 198.59 149.08 119.93 84.85 31.40 nil	$\begin{array}{r} & & \\$	$\begin{array}{c}$	$\begin{array}{c}$	165 162 156 157 157 157 157 159 162 164 165 170 172

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Time in hours.	Pressure of oxygen in mm.	<i>K</i> ₁ .	K ₂ .	K ₃ .	K4.
0	666.40				_
0.20	644.37	277	422	440	169
1.00	624.82	276	417	416	158
1.20	606.21	274	411	401	152
2.00	587.78	273	406	393	148
3.00	554.00	270	396	375	139
4.25	515.44	266	384	355	129
5.50	479.96	263	373	339	121
7.00	437.10	264	366	326	115
16.00	134.27	417	442	332	76.8
16.75	87.41	500	484	345	97.8
17.00	65.07	427*	428*	694*	764 *
17.08	56.54	473	457	719	768
17.16	46.79	543	502	756	780
17.25	34.76	667	576	816	800
17.33	18.53	962	706	915	826
17.41	nil	2427	1169	1010	800
	1				1
	(See C	urve 2. p. 1	272.)		

Expt. 4. $t = 19.6 - 19.8^{\circ}$.

* Oxidation being now very rapid, these and the following numbers indicate the progress of the reaction after 16.75 hours.

In the curves, the values of dp/dt have been plotted as ordinates, and the values of p as abscissæ. dp/dt evidently increases considerably as p diminishes. With the wide variations in the values obtained for K_1, K_2 , &c., it is clear that none of the equations hold, therefore we are not justified in supposing that the rate of oxidation is proportional either to the square root of the partial pressure of oxygen or to the partial pressure. In experiment 4, readings were taken at pressures higher than 500 mm., and it will be noticed that dp/dtdiminishes with p as far as 480 mm., after which it increases. And a glance at the figures given under K_1 show that this fall in the velocity is directly proportional to the fall in pressure. This result suggests that the reaction between phosphorus and oxygen can be divided into two stages; in the first, the velocity is directly proportional to the pressure, and in the second it increases as the pressure diminishes, but not in any simple ratio.

Oxygen under High Pressure.

In this series of experiments, the initial pressure of the oxygen was between two and three atmospheres. The apparatus was somewhat modified by bending the gauge upwards to a height of three metres; the tube leading to the pump was sealed off as soon as the last exhaustion was finished, but the oxygen generator had to be left on. Waterjackets were arranged round all parts of the apparatus out of the bath. The results are given in the following tables (p. 1273); in only one

case was the reaction continued until all the oxygen was absorbed, in the others, it was interrupted so as to determine which oxide was produced.

Similar results were obtained in both series of experiments when the oxygen was generated from potassium permanganate.

Owing to the disposition of the apparatus it was not possible to use the cathetometer, and readings had to be taken on a scale fixed to the gauge; the readings are therefore not so accurate as those of the first series. The results lead us to two remarkable conclusions. In the first place, they contradict the usual statement that phosphorus only reacts with oxygen under low pressures; the initial pressure of oxygen in experiment 2 was 2000 mm. In the second place, as K_1 , calculated from equation (1), p. 1267, is now constant, it follows that the velocity of this reaction is proportional to the pressure of oxygen, and therefore down to a certain pressure the reaction is unimolecular.

During this first stage, there is phosphorescence, but it is so feeble that it is only seen after

In the second stage (the the eye has become accustomed to darkness. more rapid period), ordinary phosphorescence appears and there is no possibility of confusing the two glows. Doubtless this very feeble glow accounts for the first stage having been previously overlooked,

Pressure in mm.

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Time in hours.	Pressure of oxygen in mm.	K ₁ .	Time in hours.	Pressure of oxygen in mm.	<i>K</i> ₁ .
$egin{array}{c} 0 \\ 1 \\ 2 \\ 6 \\ 10 \\ 14 \end{array}$	$ \begin{array}{r} 1319 \cdot 2 \\ 1273 \cdot 7 \\ 1231 \cdot 6 \\ 1103 \cdot 0 \\ 975 \cdot 8 \\ 874 \cdot 5 \\ \end{array} $	156 149 129 131 127	18 20 21 22 24 25	774.5730.0708.4687.4639.3615.3	128 128 128 129 131 132

Expt. 1. $t = 14 - 15.0^{\circ}$.

Expt. 2. $t = 13 - 14^{\circ}$.

Time in hours.	Pressure of oxygen in mm.	<i>K</i> ₁ .	Time in hours.	Pressure of oxygen in mm.	<i>K</i> ₁ .
0 4·09 9·00 14·10 18·00 20·10 22·00 24·00 26·00	1949 •2 1887 •3 1809 •8 1728 •1 1663 •6 1629 •7 1602 •0 1573 •9 1544 •8	342 358 370 382 386 386 386 387 388	28.0 31.5 36.0 38.0 40.0 42.0 44.0 46.0	1513 ·2 1468 ·4 1410 ·1 1892 ·3 1368 ·5 1345 ·0 1324 ·7 1301 ·5	392 390 385 384 384 384 384 382

for it is generally assumed that oxidation ceases as soon as the ordinary and relatively bright glow stops. Moreover, it is an essential condition to success that the surface of the phosphorus shall be quite clean, and one can only rely on fulfilling this condition by redistilling the phosphorus *in vacuo*, as was done in these experiments.

Phosphorus is extraordinarily sensitive to surface contamination, which either greatly retards oxidation or altogether stops it.* On one occasion, the distillation had not gone quite smoothly and a certain amount of the liquid portion boiled over into the bulb. When oxygen was let in under 1900 mm. pressure, there was a slight action at first, the pressure falling about 60 mm., then the action stopped altogether and did not start again even when the temperature was

* John Davy (*Edin. New Philos. Journ.*, 1833, **15**, 48) found that when phosphorus was kept in oxygen under the atmospheric pressure for several hours, the volume was not much diminished, and Müller (*Ber.*, 1870, **3**, 84) sealed up phosphorus with oxygen in a flask, left it for $2\frac{1}{2}$ months, and then opened under water and found no change in volume. In both cases, there was no doubt a protective film on the surface.

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raised to 26°. The apparatus was opened for a moment to let out the excess of oxygen, and then sealed up and more oxygen generated until the pressure was restored to 1900 mm.; this time the action was normal. Probably the sudden release of the pressure altered the surface of the phosphorus sufficiently to allow the oxidation to proceed.

Preliminary Examination of the Oxide formed during the First Stage.

This oxide is perfectly white, there being no buff-coloured substance produced here as in the next stage. When heated in vacuo, a few white crystals sublime, the rest of the substance breaking up into a white, crystalline sublimate, less volatile than the first, and a red residue. Finally, this red residue largely disappears, being apparently changed to ordinary phosphorus when heated for a longer time. The white, crystalline sublimate seems to be phosphorus tetroxide, and the red residue, amorphous phosphorus. On treating with water, the oxide only slowly dissolves; the solution reduces mercuric chloride and silver nitrate and gives a white precipitate with magnesia mixture, which, when examined under the microscope, is seen to differ altogether in crystalline form from the precipitate obtained with either of the three phosphoric acids, and is apparently identical with that obtained from a solution of phosphorous oxide. But the oxide does not melt on heating, whereas if it were phosphorous oxide, as the above reactions indicate, it should melt at 22°. I hope shortly to be able to determine the precise nature of the substance.

Discussion of the Results. First Stage.—The reaction being unimolecular, the first action would naturally be $P_4 + O_2 = P_4 O_2$, and no doubt this oxide may have a transient existence. A little reflection will make it evident, however, that the reaction will still appear unimolecular if the $P_4 O_2$ is oxidised at an infinite velocity to $P_4 O_4$, and this also at an infinite velocity to a higher oxide. If one of the two latter velocities is not infinite, but only somewhat greater than the first velocity, it ought to be possible to isolate the intermediate oxide, since this would not be oxidised quite so fast as it was produced, but only some short time afterwards.

Walker (*Proc. Roy. Soc. Edin.*, 1898, 22, 22) draws attention to Harcourt and Esson's investigation of two unimolecular reactions proceeding simultaneously. A substance A is transformed into C through an intermediate compound B; if at a time t, x is untransformed, y is in the intermediate state, and z in the final state, then x + y + z = A. Suppose the velocity constant $A \longrightarrow B$ be m, and $B \longrightarrow C$ be n, then at time t the rate of diminution of x is given by the equation -dx/dt =mx, and the rate of increase of z by dy/dt = ny: it can then be shown that

$$z = A\left\{1 + \frac{n}{m-n} \cdot e^{-mt} + \frac{m}{n-m} \cdot e^{-nt}\right\} \quad . \quad . \quad (7).$$

In the special case when one of the coefficients, n for example, becomes infinitely great, this expression reduces to $z = A(1 - e^{-mt})$, the ordinary equation for a unimolecular reaction. Walker calculates values for z in his hypothetical reaction, assigning different values to m and n, and shows that the "constant" K, as calculated on the assumption that the reaction is single and unimolecular, would increase in value, rather rapidly at first, more slowly afterwards. Now the approximately constant values obtained for K seem to indicate that all the reactions but one proceed at so great a velocity that there is no prospect of isolating the other intermediate oxides which may be supposed to be formed.

It is, of course, quite possible that the constancy of K is only accidental, as is the case with an apparent constant discussed in the sequel (p. 1282).

Second Stage.—The intermediate oxide, whatever it is, obtained during the first stage evidently oxidises during the second stage, since the final product is phosphoric oxide. With this change proceeding at a finite velocity, the total action will be expressed by an equation which, at its simplest, will be of the form of equation 7, but probably will be more complex. It is not surprising, then, that no simple law could be discovered underlying the results at low pressures. Moreover, since the velocity tends to increase as the pressure diminishes with the progress of the reaction, it is hardly possible to assume that the system remains strictly isothermal, and no doubt the very rapid final rates in experiments 1 to 4 (pp. 1269, 1270, 1271) are due to a rise in temperature. This would also explain the presence, in the oxide obtained, of a small quantity of a buff-coloured substance, apparently amorphous phosphorus.

Influence of an Inert Diluting Gas.

As it was necessary to ascertain how the velocity of oxidation would be affected by the presence of an inert gas, nitrogen was introduced as a diluent in the following experiments:

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Expt. 1. Pressure of nitrogen = 165.2 mm. $t = 19.2^{\circ}$.		Exp Pressure of nitr $t = 1$	ot. 2. rogen = 240 mm. 3.6°.
Time in minutes.	Pressure of oxygen in mm.	Time in minutes.	Pressure of oxygen in mm.
$\begin{array}{c} 0\\ 295\\ 365\\ 440\\ 515\\ 590\\ 635\\ 695\\ 725 \end{array}$	$\begin{array}{c} 300 \cdot 93 \\ 194 \cdot 99 \\ 165 \cdot 61 \\ 132 \cdot 93 \\ 99 \cdot 48 \\ 68 \cdot 79 \\ 56 \cdot 31 \\ 44 \cdot 27 \\ 39 \cdot 66 \end{array}$	0 45 90 135 180 225 270 315	393.42 327.14 247.54 160.05 91.93 46.93 19.38 6.30

Sulphuric acid was used as drying agent.

The curve given is that for experiment 2; the other is precisely



similar in form, but the turning point is at an oxygen pressure of about 120 mm. In experiment 2, the curve turns at 216 mm.; in a

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third experiment, the pressure of the nitrogen was 56 mm. and the curve began to turn when the oxygen pressure had fallen to about 20 mm.; the return always seems to begin when the oxygen pressure has fallen somewhat below the nitrogen pressure. Instead of increasing continuously to the end, the velocity reaches a maximum and then diminishes fairly rapidly.

This result is not difficult to understand. If a tube filled with air contains some phosphorus at the bottom, the oxygen in the lower layers of the air will be absorbed and there will be a steady drift of oxygen down the tube. This drift is, however, retarded by the nitrogen, and the retarding effect becomes greater as the pressure of the oxygen becomes less: in other words, the rate of oxidation diminishes as the partial pressure diminishes, because the oxygen has a greater difficulty in reaching the phosphorus. At a certain point, the retarding effect of the nitrogen more than counterbalances the acceleration connected with a fall in the partial pressure of oxygen, and from this point onwards the whole velocity diminishes.

The oxide formed is white, and the absence of any buff-coloured substance is no doubt connected with the fact that the action never proceeds very rapidly.

THE OXIDATION OF MOIST PHOSPHORUS.

This is the most commonly occurring case of the oxidation of phosphorus, and the more striking facts in connection with it have been known for a long time. There are some notable differences between this and the preceding case. Action only begins when the pressure is reduced below a certain amount, and ozone and hydrogen peroxide are invariably produced; if nitrogen is present, ammonium nitrate and nitrite are formed as well. Recently, certain emanations from moist oxidising phosphorus have been discovered; whether these are due to the special physical properties of the cloud formed by the oxidation products or whether they are definite rays coming from the phosphorus itself is not settled. Harm and also Elster and Geitel (Phys. Zeit., 1903, 16, 457) incline to the latter opinion, Schmidt (Ann. Phys., 1902, 10, 704) to the former. Phosphorus, as dried in the foregoing experiments, does not seem to have been the subject of any investigations of this kind.

Side Reactions.

Ozone and Hydrogen Peroxide.—Schönbein and Schmidt (loc. cit.) proved the presence of these substances among the oxidation products, and this has been confirmed by later workers (Leeds, Chem. News, 1879,

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40, 70; and Wenzell, Pharm. J., 1883, [iii], 14, 24). Kingzett. indeed (Trans., 1880, 37, 792), claimed to have found a regular connection between the amounts of hydrogen peroxide and ozone, but the difficulty of analysing the mixture must have been considerable. McLeod could not obtain any regular results (Trans., 1880, 37, 118). The substances are usually accounted for by supposing that during oxidation some oxygen molecules are dissociated and the oxygen atoms form ozone and hydrogen peroxide. Ostwald (Zeit. Phys. Chem., 1900, 34, 248) gives some theoretical objections to this view, the general nature of which is that ozone, having a higher oxidation potential than the oxygen from which it was formed, can only be produced by the addition of energy. But the chemical energy of one reaction is not available for another and totally different reaction, and so the energy degraded during the oxidation of phosphorus cannot be utilised for producing ozone. He assumes that a higher peroxide must first be formed, subsequently breaking up into ozone and the stable oxide actually produced, and represents the reaction :

$$nP + mO_2 = P_nO_{2m} = P_nO_{(2m-3r)} + rO_3$$

thus bringing the action into line with the work done by Bach, Engler, and Wild on autoxidation. Now Boche (*Ber.*, 1873, 6, 439) states that the oxidation of phosphorus gives rise to an oxide which generates hydrogen peroxide in contact with water. 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.

Doubts have sometimes been raised as to whether the so-called ozone is really ozone or not. I find it possesses the following properties: (1) it passes, without condensation, through a tube 18 inches long cooled with solid carbon dioxide, (2) it rapidly destroys india-rubber, (3) it acts on mercury precisely as ozone does.

There seems to be little doubt that it is actually ozone.

Ammonium Nitrite and Nitrate.—I find that both of these are present, although only in small amount.* The greatest care was taken to exclude ammonia, and it is difficult to account for their formation; the case does not stand quite by itself, however, for Norman Smith and I have found them in the products of oxidation of zinc and iron in moist air. Hydrogen peroxide is also formed, and the only differences between the oxidation of the metals and that of phosphorus are the production of ozone and the velocity of reaction.

* So small as not to vitiate Lindemann's method of analysing air by means of phosphorus (Zeit. Anal. Chem., 1879, 18, 158).

Velocity of Oxidation.

These experiments were carried out in the same way as the corresponding experiments with dry oxygen, the only difference being that water was substituted for sulphuric acid in the tube C.

Experiments under High Pressures.—As a rule, no reaction took place even after six months. In a few cases, reaction began but soon stopped, and the phosphorus became coated with a white substance which neither deliquesced nor showed any sign of change even after prolonged contact with the moist oxygen. But when the temperature was raised, ignition took place. This oxide is being investigated.

The cessation of action between phosphorus and moist oxygen when the pressure exceeds a certain amount is often quoted as an instance of false equilibrium. It was noticed in the experiments on dry phosphorus that reaction does not cease if the system is fairly dry; all the phenomena are, however, consistent with the idea of false Duhem supposes that there is a resistance to the equilibrium. reaction, and likens the system to a rough inclined plane bearing a weight at the end which is gradually being raised. If there were no friction, the weight should begin to move directly the end is lifted, but, as a matter of fact, the plane has to be inclined at a certain angle before any motion begins. He considers that this unexpected equilibrium is analogous to false equilibrium in chemical reactions. In the present instance, water vapour is the retarding agent. It is unfortunate that the velocity of oxidation of dried phosphorus cannot be represented by any simple expression, for it would not be difficult to put in a factor to stand for the friction effect. Some connection might then be traced between the amount of water vapour present and the pressure at which the reaction begins.

The curve (p. 1280) shows a retarding effect at work in the early part of the oxidation, followed by the rapid increase in velocity noted in the experiments with dry oxygen. When oxidation first begins, the luminosity is seen in only one or two places on the phosphorus, and not until nearly the end does the whole mass glow.

In trying to interpret these observations, the following possibilities have been considered: (a) a possible chemical action of water vapour on phosphorus. (b) A possible physical action of water vapour in modifying or protecting the surface of phosphorus. (c) The dynamical effect of an inert diluting gas.

(a) A Possible Chemical Reaction.—Some phosphorus was distilled into an exhausted apparatus containing water as in the previous experiments, the apparatus sealed off and left in a warm place (18°) in the dark for two months, the gauge being read daily. There was no increase of

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<i>Expt.</i> 1. <i>t</i> =19—19·1°. Pressure of aqueous vapour, 16·35 mm.		Expt. 2. $t = 23^{\circ}$. Pressure of aqueous vapour, 20.9 mm.		
Time in minutes.	Pressure of oxygen.	Time in minutes.	Pressure of oxygen.	
$\begin{array}{c} 0\\ 30\\ 60\\ 90\\ 120\\ 150\\ 275\\ 305\\ 365\\ 395\\ 425\\ 440\\ \end{array}$	335.62 281.51 250.07 225.28 203.77 184.72 109.15 92.25 53.93 32.57 8.85 nil	0 10 20 30 40 50 60 70 80 90 100 110	327 ·14 294 ·40 268 ·74 246 ·62 227 ·00 209 ·64 193 ·40 178 ·07 163 ·18 149 ·38 136 ·39 121 ·15	
(See Curve 4.)		120 130 140	54 25 50·35 nil	







pressure and therefore no gas was formed. At the end of the time, the surface of the phosphorus was carefully examined, but no change in appearance could be detected

Without further evidence, we do not seem justified in assuming that any chemical action takes place.

(b) A Possible Physical Action.-The part of the apparatus containing

the phosphorus was then surrounded by a freezing mixture, air was admitted, the water tube cut off, and a calcium chloride tube put into its place. The air was exhausted and oxygen passed in until the atmospheric pressure was attained. Inasmuch as the water was now removed and dry oxygen was present, oxidation should have gone on just as in the earlier experiments if the phosphorus had been unaltered by contact with the water vapour, but as a matter of fact no oxidation took place under this pressure until some months had elapsed. Water vapour does, therefore, in some way form a protecting film on the phosphorus surface.

(c) The Effect of an Inert Gas.—This does not seem to be great until almost the end of the reaction, and if 56 mm. of nitrogen only altered the curve near its end-point, it is doubtful whether 20 mm. of water would do more.

There is, of course, always the possibility that in presence of water vapour there may be a complete change in the mode of oxidation and that these results cannot be correlated with those on p. 1269. My experiments, however, do not favour this idea. If instead of 20 mm. pressure of water vapour only 4 mm. are employed, the velocity curve does not differ sensibly from those obtained for dry oxidations.

Two experiments are given, in which dilute sulphuric acid (44 per cont.) replaced the water in the apparatus.

Exp	rt. 1.	$Exp t = 11^{\circ}.$ Tens vapour,	ot. 2.
t = 9°. Tension of	2 aqueous vapour,		ion of aqueous
4.2	1 mm.*		4·6 mm.
Time in minutes.	Pressure of oxygen.	Time in m inutes.	Pressure of oxygen.
0	467.27	0	464.63
15	424.97	30	429.80
30	381.68	60	389.53
45	332.64	90	348.44
60	276.65	120	300.43
75	.209.67	150	248.32
90	112.83	180	185.47
97	nil	210	97.60
(See Curve	5, p. 1282.)	225	nil

* Sorel, J. Soc. Chem. Ind., 1890, 9, 175.

In experiment 2, the apparatus was filled to a pressure of 760 mm., in experiment 1 to 520 mm. only. Moreover, if oxygen fully saturated with water vapour is used, but the experiment conducted in such a way that water vapour has not had access to the phosphorus for any great length of time before oxidation begins, the curve again resembles those obtained with dried gases.

The modifying effect of water vapour can, I think, be explained entirely by the surface protection noted under (b). This would, in the first instance, tend to prevent oxidation; when it does start, it is at some point where the protection is weak, consequently oxidation is at first purely local. As the pressure diminishes, the velocity



increases, and the heat developed causes the reaction to spread until finally the whole mass of phosphorus is being acted on.

The appearance of the glow supports this view, which is also in accordance with the fact that the retarding effect is greatest during the earlier part of the oxidation.

Ewan and Ikeda both state that when moisture is present the velocity of oxidation in mixtures containing nitrogen is proportional to the partial pressure of oxygen, which, according to Ewan, is not the case when moisture is absent. This would suggest that the process of oxidation is different in the two cases of presence and absence of moisture. However, water vapour retards oxidation at the beginning, and nitrogen restrains it at the end of the reaction, so that if both retardations take place in a given oxidation, the curve expressing the resultant velocity might easily reduce to a straight line passing through the origin.

Conclusions.

(1) A small quantity of water is necessary for the oxidation of phosphorus, and the reaction proceeds most rapidly when that quantity is present which is left after drying with sulphuric acid. When much water vapour is present, the action is considerably retarded.

(2) The formation of ozone and hydrogen peroxide requires the presence of excess of water; these substances are not direct products of the reaction between phosphorus and oxygen.

(3) Moderately dried phosphorus and oxygen react under all the pressures tried, and the phenomena of "false equilibrium" are not seen. The reaction may be divided into two stages: in the first, oxidation is slow and accompanied by a very feeble glow, the action being apparently unimolecular. The oxide formed is now under investigation. The second stage begins when the pressure falls below about 500 mm.: oxidation is continually accelerated until all the oxygen is absorbed, but no simple expression could be found connecting the velocity of the reaction with the pressure of oxygen. The glow is very bright and phosphorus pentoxide is formed. No satisfactory explanation of the phenomena of the second stage can yet be offered.

(4) When an inert gas, such as nitrogen, is present, the phenomena are substantially the same, but the acceleration of the second period ceases after a time and a retardation sets in. This is explained on a purely mechanical hypothesis.

(5) When phosphorus oxidises in moist oxygen, the reaction differs from that taking place in dry oxygen in the following respects:

(a) The oxidation does not begin until the oxygen pressure is less than about 500 mm.; when it does take place, it is slower, and is much retarded during the earlier part of the reaction. The retardation is explained as being due to a protective film formed in some, probably physical, manner by the water on the phosphorus.

(b) Ozone and hydrogen peroxide are produced, and ammonium nitrite and nitrate also, in the presence of nitrogen. None of the theories at present held completely accounts for these observations.

If the vapour pressure of water is 4-5 instead of 16-20 mm., the velocity curve does not greatly differ from that obtained in absence of water. And the difference observed in presence of the larger

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quantity of water can readily be explained by assuming the formation of the protective film. There is no necessity to suppose that the primary reaction between the phosphorus and oxygen differs in the two cases.

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