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XVIII. *Combustion in Dried Oxygen.*

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Communicated by Professor H. B. Dixon, *F.R.S.*

The chemical changes occurring in combustion hold such an important position, not only in the history and advance of chemical science, but also in the applications of science to industry, that special interest is attached to the discovery of the nature and order of the chemical changes involved. The phenomena presented by the oxidation of carbon, sulphur, and phosphorus have been studied by chemists as typical of those which are found in other processes of burning. With the object of determining the conditions necessary for the oxidation of these three substances, I began in 1884 an investigation, the results of which are described in the following paper. That water vapour might play an important part in such actions seemed very probable. The interesting facts brought to light by my former tutor, Professor H. B. Dixon, with regard to the oxidation of carbon monoxide (' Phil. Trans.,' 1884) made it seem likely that water vapour might exert as strong an influence on other combustions as he has shown it does on that of carbon monoxide. It was suspected some years ago that the combustion of carbon is affected by the presence or absence of moisture. In 1871 M. Dubrunfaut read a paper before the Académie des Sciences describing some experiments bearing on this point. He had performed combustions of sugar-charcoal in oxygen dried by strong sulphuric acid, and found that the carbon did not undergo combustion as readily as it did if the oxygen was moist. He ascribed the incompleteness of the oxidation of the carbon to the presence of moisture which was inaccessible to our reagents, that is, moisture which did not cause a weighed sulphuric acid tube through which it was passed, to increase in weight. A few weeks later M. Dumas, who had determined the equivalent of carbon by burning a weighed quantity of pure graphite in pure oxygen, repeated the experiments, and, by using a large quantity of the partially dried oxygen, succeeded in burning the whole of a small quantity of graphite.

In my first experiments on the combustion of carbon in oxygen,* wood charcoal was employed. It was freed from hydrogen by heating in a current of chlorine for several hours. It was placed in glass tubes, into which phosphorus pentoxide had been

* ' Chem. Soc. Journ.', 1885, *Trans.* p. 349.

previously introduced, the two substances being separated by a disc of platinum foil. The latter did not fit so closely as to prevent the free diffusion of the gaseous contents of the tubes. Oxygen dried by sulphuric acid was then passed through the tubes, which were then sealed at both ends. Experiments have shown that the long contact of phosphorus pentoxide with gases has an immeasurably greater drying effect than the mere passage of the gases through tubes containing that substance. After standing for some days each of these tubes was heated, side by side with a similar tube containing charcoal in moist oxygen, by the flame of a large Bunsen burner. The moist carbon always burnt with the scintillation characteristic of such a combustion, but the dry carbon remained apparently unaltered. On analysis, however, it was found that a certain quantity of carbon had been burnt. The following Table gives the results of the analysis of the gaseous contents of the tubes, after the carbon had been heated to redness in them for about two minutes.

	I.		II.		III.		IV.		V.		VI.	
	Wet.	Dried for 1 week.	Wet.	Dried for 2 weeks.	Wet.	Dried for 4 weeks.	Wet.	Dried for 8 weeks.	Wet.	Dried for 12 weeks.	Wet.	Dried for 16 weeks.
Carbon dioxide .	50·1	15·4	51·0	19·0	45·3	14·1	23·3	12·5	58·8	15·8	52·4	17·8
Carbon monoxide	22·2	20·6	31·2	14·8	32·5	27·8	60·0	27·5	23·2	24·2	25·2	16·5
Oxygen	..	41·3	..	46·1	..	28·2	..	39·0	..	33·3	..	45·0
Nitrogen . . .	27·6	22·6	17·7	20·0	22·1	29·8	16·6	21·0	17·9	26·6	22·3	20·6

It will be noticed that in four out of these six experiments more than half the oxygen was left uncombined with the carbon, whilst none remained in the wet tubes. The comparatively large quantities of carbon monoxide produced are striking when we consider that the temperature was not high, and that the reduction of carbon dioxide by carbon is never rapid. These results formed the starting point of an investigation in which the precautions taken to ensure the purity and dryness of the substances used were made much more elaborate.

The carbon used in the later experiments was in the form of charcoal. It was prepared by heating sugar in a silver dish to a bright red heat. The porous mass was broken up and finely powdered. It was transferred to a combustion tube, and heated to redness for three days in a current of pure chlorine dried by sulphuric acid, in order to eliminate hydrogen from the powder. The charcoal was washed by decantation with distilled water until the washings gave no opalescence with silver nitrate. To free it from occluded hydrochloric acid, it was placed in a hard glass tube sealed at one end, while at the other end was placed a stick of solid potash. The tube was then exhausted by a Sprengel pump, and the end containing the carbon was heated to dull redness for several days, the vacuum being constantly maintained. Hydrochloric acid gas was evolved, partly absorbed by the potash, but at first passing over in such quantities that it could be collected from the air-pump. After this treatment

the carbon was considered sufficiently pure for the experiments. It was kept in a small stoppered bottle, but, as this involved exposure to a small quantity of air, it was thought advisable before the carbon was used for the preparation of each experiment that the portion taken should be heated to redness in a vacuum. This served not only to dry it, but also to free it from occluded oxides of carbon which are products of its slow combustion in air at ordinary temperatures.

The oxygen was prepared by heating pure potassium chlorate, and was stored in gas pipettes over previously boiled mercury. In the gas were placed plugs of phosphorus pentoxide. These plugs were made thus :—A piece of glass tubing, 1 cm. in diameter, and a longer piece of glass rod, exactly fitting it, were heated to dry them thoroughly. The tube while still warm was pushed to the bottom of the bottle containing the pentoxide, and the portion of the latter so introduced was compressed by forcing the glass rod into the tube like a piston. Both tube and rod were then removed from the bottle, with the plug almost entirely protected from the air. The tube was then quickly plunged under the mercury, through the tubulure of the pipette, and the piston pressed down. The plug was thus pushed out of the tube, and rose through the mercury into the oxygen which was to be dried. This plan of dealing with the phosphorus pentoxide, in the form of a compact cylinder, was extremely useful when it was necessary to introduce it into glass tubes which were to be drawn out in the blow-pipe flame. If only a small quantity of the oxide adheres to the portion of the glass to be heated, it diminishes the ductility to a remarkable degree, and renders it extremely brittle.

Carbon heated in contact with Platinum.

A mixture was made of platinum black (previously heated to redness in a vacuum) and the pure charcoal. A hard glass tube was slightly contracted in the middle, and heated in a current of dried air to dull redness, to get rid of the moisture which clings so tenaciously to glass. On one side of the constriction was introduced the mixture of platinum and carbon, and on the other plugs of phosphorus pentoxide. Oxygen was passed through the tube and the ends sealed. The oxygen was left drying for six weeks. At the end of this time the part of the tube containing the mixture of carbon and platinum was heated to redness for three minutes with no sign of visible combustion. Analysis showed that the tube now contained—

Carbon dioxide . . . 27 per cent.
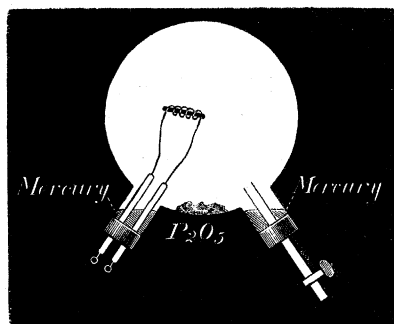Oxygen . . . . . . 73 „

A second experiment, in which the oxygen was dried for three weeks, and the mixture of carbon and platinum was heated for four minutes, gave—

Carbon dioxide . . . 34 per cent.
Oxygen . . . . . . 66 „

The quantities of carbon burnt in these two experiments do not differ greatly from the quantity of carbon burnt under similar conditions when no platinum was present. There is, however, this important difference between the two cases, that in the presence of platinum only carbon dioxide is produced.* In the absence of platinum varying quantities of carbon monoxide were formed, generally exceeding in amount the carbon dioxide produced at the same time.

A third experiment was made with carbon in contact with platinum. The charcoal was in the form of a rod, about 4 cm. in length. It was enclosed in a coil of fine platinum wire, which had been previously freed from hydrogen by heating to redness in oxygen. The ends of the coil were attached to thicker platinum wires, which were sealed into two pieces of quill tubing. These passed through two holes in an india-rubber stopper which fitted into the neck of a small flask (fig. 1). The flask

Fig. 1.

contained pure oxygen, dried by plugs of phosphorus pentoxide placed in the flask. A small quantity of mercury covered the stopper, to prevent diffusion of water vapour through its mass. The gas was left drying for fourteen days.

The platinum coil was heated by an electric current to a bright red heat. The carbon did not catch fire, and the glow disappeared directly the current was stopped. With a stronger current, the platinum was heated nearly to whiteness; the carbon showed visible combustion for two seconds, after which the glow died out. On analysing the contents of the globe after the experiment, more than half the gas was found to be oxygen.

A similar experiment was tried with a rod of carbon in moist oxygen. On raising the temperature to dull redness by means of the heated wire, the carbon caught fire, and, although the current was immediately broken, there was no cessation of the combustion until the rod was entirely consumed.

These results point to the conclusion that the contact of platinum does not cause the union of dry carbon with dry oxygen, but only influences the products of combustion.

* It has been proved that dry carbon monoxide and oxygen unite readily without flame in presence of red-hot platinum (DIXON and LOWE, "Chem. Soc. Journ.', 1885, *Trans.* p. 575).

The Products of Combustion of Charcoal in Oxygen.

In the course of the experiments on the combustion of carbon in dried oxygen, a gas-holder was constructed to contain oxygen dried by phosphorus pentoxide. The only liquid which could be used for driving out the gas was mercury, and, as the amount of gas required was about eight litres, its use would have been inconvenient. The following apparatus was fitted up.

Fig. 2.
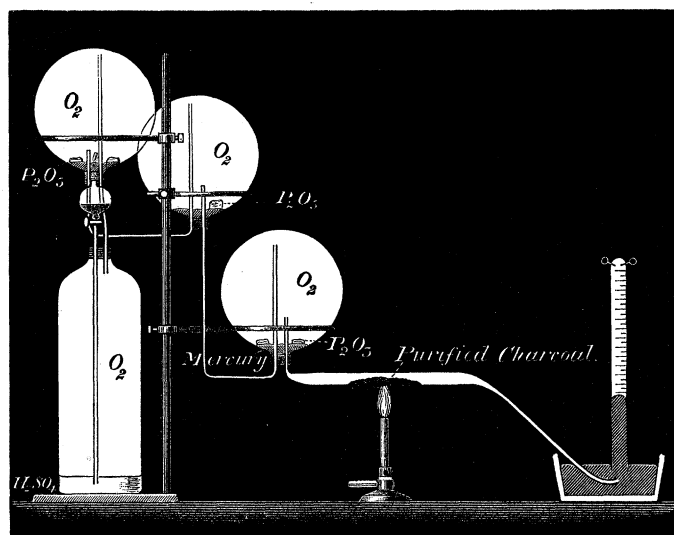
A large bottle was graduated and fitted with an india-rubber stopper, through which a large tap-funnel was passed. Through another hole in the stopper a narrow upright tube was fixed. This passed to the top of an inverted two-litre flask, also provided with an india-rubber stopper. A bent tube also passing through this stopper was connected with a second flask arranged in the same way as the first. A third flask, similarly fitted, completed the gas-holder. It resembled three inverted wash-bottles, with the exit tube of one connected with the pressure tube of the next. The whole, including the large bottle, was heated for several hours by Bunsen burners playing on the sides, while a current of air, dried by sulphuric acid, was drawn through the apparatus.

In order that no moisture should be given off from the india-rubber stoppers in the three flasks, each was covered with a little mercury previously boiled. On the surface of the mercury in each flask five or six plugs of phosphorus pentoxide were placed. A current of oxygen was passed through six long, nearly horizontal, tubes filled with concentrated sulphuric acid, and then through the apparatus described above. After passing for an hour a sample of the gas was collected as it issued from the last flask. It was found to be pure oxygen. A hard glass tube containing dried charcoal was drawn out at both ends. One end, bent upwards, was passed through the opening in

the stopper of the third flask ; the other end was sealed.   A small quantity of boiled sulphuric acid was poured into the bottle through the stoppered funnel, so that the pressure of the gas during its drying might be greater than the atmospheric pressure. The gas was thus dried, partly by phosphorus pentoxide, and partly by sulphuric acid. Since the connecting tubes were narrow, only a slow diffusion of slightly moist gas from the bottle containing strong sulphuric acid could take place into the flasks.   The gas was thus thoroughly dried in the second and third flasks.   The oxygen used in the experiment was taken from this third flask, though the pressure used to drive it out was derived from the sulphuric acid poured into the large bottle.   The apparatus was left to dry for four days.

Experiment I.—The sealed end of the tube having been broken off under dried mercury, the carbon was heated to dull redness in a stream of the dried gas.   At first it glowed a little.   The current was stopped.   A blue flame was seen to run along the tube from the heated point to the end.   This could only be due to carbon monoxide.

Experiment II.—As it was evident that either the charcoal or the glass was not quite dry, the tube, still connected with the oxygen flask, was sealed at its open end, and allowed to dry for another week, gentle heat being occasionally applied.   At the end of this time the sealed end of the tube was broken under mercury, previously dried.   The part containing the charcoal was heated as before with a Bunsen burner. This time no glowing was seen, although 200 c.c. of oxygen was rapidly passed over the red-hot charcoal.   After this a sample of 27·5 c.c. of the gas was collected.   It was analysed and found to contain—

	c.c.	Per cent.
Carbon dioxide	1·4	5·0
Carbon monoxide	11·0	40·0
Oxygen	15·1	54·9
	27·5	99·9

Experiment III.—The apparatus was allowed to stand for another week, and then the charcoal was raised to bright redness with a gas blow-pipe.   No visible combustion occurred ; 29·6 c.c. of gas was collected.   The analysis gave—

	c.c.	Per cent.
Carbon dioxide	·6	2·2
Carbon monoxide	11·8	39·5
Oxygen	17·2	58·1
	29·6	99·8

These analyses are very striking, showing that a large quantity of carbon monoxide is produced when carbon is heated in a current of oxygen, even when the oxygen is in excess.   They seem to point to the conclusion that carbon burns first to carbon

monoxide, and that this, unless prevented by dryness, as in this case, or by some other influence, then produces carbon dioxide.

This conclusion is strengthened by the fact that when a piece of charcoal is heated in a rapid stream of ordinary oxygen a long flame is seen to issue from the glowing solid in the direction of the current of gas. This is probably the second stage in the burning of the charcoal.

It has been shown (C. J. BAKER, 'Chem. Soc. Journ.,' 1887) that a small quantity of carbon monoxide is produced by the slow absorption of oxygen by charcoal. This was given out by heating to 45° in vacuo. The amount was not more than 5 c.c., given out by heating half a gram of charcoal for two hours. Though such a small amount was not likely to vitiate an experiment made at more than atmospheric pressure, and lasting not more than two minutes, it was thought advisable to use precautions to obviate any possibility of error from this source. The following method was then tried.

The oxygen was contained in a gas pipette with a stop-cock. Phosphorus pentoxide was introduced, and the gas was left drying for a week. The aperture of the pipette was connected by a piece of dried and paraffined india-rubber tubing with the tube containing the carbon. In this india-rubber tube phosphorus pentoxide was placed. The carbon had been heated to redness *in vacuo* to free it from any carbon monoxide which might have been occluded. The tube containing it was drawn out in the middle, and phosphorus pentoxide placed in the part remote from the pipette. To prevent the formation of carbon monoxide in the charcoal while the oxygen was drying, the tube was exhausted as completely as possible and the free end drawn out to a point and sealed.

Fig. 3.
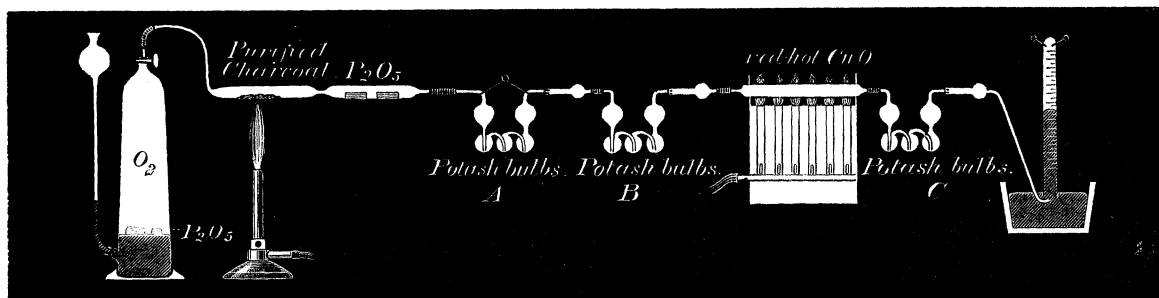
The oxygen was to be driven out by mercury which had been boiled and cooled in an atmosphere dried by sulphuric acid. After a week's drying the gas was admitted to the vacuous tube. The sealed tip was broken and connected with a set of GEISSLER'S potash bulbs. These would absorb the carbon dioxide produced. Next in series was another set of weighed potash bulbs which would indicate whether all the carbon dioxide had been absorbed by the first set. Connected with these bulbs was a hard glass tube containing copper oxide heated to redness in a small gas furnace. In this

tube any carbon monoxide which was produced in the combustion would be converted into carbon dioxide.   Next in the series was a third set of potash bulbs to absorb this carbon dioxide.   The calcium chloride tube of this third set of bulbs had a conducting tube attached to it which dipped under mercury contained in a trough.   Here the residual gas was collected.

The carbon was raised to a red heat by a Bunsen burner.   No visible combustion took place.   Oxygen was passed over it at the rate of about 20 bubbles a minute. The gas collected over the mercury was at first a mixture of oxygen and nitrogen. The latter was derived from the air contained, at the beginning of the experiment, in the bulbs and the copper oxide tube.   The gas collected towards the end of the experiment was pure oxygen.

When all the oxygen had been driven over the charcoal, the potash bulbs were disconnected, filled with air, and weighed.   The second set, which were used to test the efficacy of the first set, had not increased in weight.   From the increase in weight of the first set, the weight of carbon dioxide produced in the combustion was found. The increase in weight of the third set gave the weight of carbon dioxide produced by the oxidation of the carbon monoxide formed in the combustion.   The analysis of the gases so found yields the following results :—

Carbon dioxide	1·7
Carbon monoxide . . .	27·8
Oxygen (by difference) .	70·5
	————
	100·0

These striking results are confirmed by the analyses of the gases contained in sealed tubes after charcoal had been heated in dried oxygen, mixed with nitrogen.

	Dried for 1 week.	Dried for 4 weeks.	Dried for 8 weeks.
Carbon dioxide . . .	15·4	14·1	12·5
Carbon monoxide . .	20·6	27·8	27·5
Oxygen	41·3	28·2	39·0
Nitrogen	22·6	29·8	21·0

That this carbon monoxide was not produced by the reduction of carbon dioxide by charcoal was shown by a series of three experiments, described later.

It was thought that, if a rapid current of air were passed over charcoal heated to a temperature below the ignition point * of carbon monoxide, the carbon monoxide, if produced, might be swept away from the area of combustion before it was oxidized.

The air used in the experiment was freed from water vapour by passing through

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* MM. MALLARD and LE CHATELIER found that a mixture of carbon monoxide and oxygen ignited at about 650° C., though gradual union took place at 400°.   ('Annales des Mines,' vol. 4, 1883.)

a tube of fused calcium chloride, and from carbon dioxide by a wash-bottle of strong potash. The purified charcoal was placed in a thick, hard glass tube (fig. 4) : with this was connected an apparatus for analysing the gases by weight similar to that used in the last experiment. Instead of the conducting tube dipping under mercury, a wash-bottle, not shown in the diagram, was connected with the last set of potash bulbs. This contained a solution of pyrogallic acid. A small tube of potash solution was placed upright in the bottle. By tilting the flask, and so upsetting the potash into the pyrogallic acid, it could be seen at any moment of the experiment whether all the oxygen was being used up by the carbon.

Fig. 4.
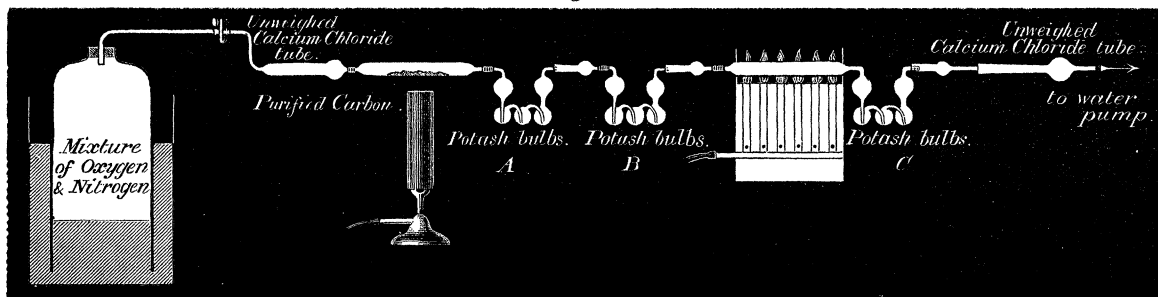
The carbon dioxide produced by the combustion is absorbed in bulbs A. Bulbs B did not increase in weight, showing that the absorption in A was complete. Bulbs C absorb the carbon dioxide formed by the carbon monoxide produced in the combustion.

The air was drawn through the whole apparatus by means of a water pump. The rate was kept constant, so that 30 bubbles per minute passed through the bulbs.

Experiment I.—The temperature of the carbon was about 500°. It was regulated so that some lead chloride placed in a similar tube by the side of the carbon tube was just melted.

Percentage of carbon dioxide produced . . . 88·2
„   carbon monoxide „ . . . 11·7
——
99·9

Experiment II.—Temperature of carbon rather lower.

Carbon dioxide . . . . 82·1
Carbon monoxide . . . . 17·8
——
99·9

Experiment III.—Temperature of carbon about 400° (m.p. of lead iodide).

Carbon dioxide . . . . 63·24
Carbon monoxide . . . . 36·76
——
100·00

Experiment IV.—The carbon was placed in a U-tube, which was heated in the vapour of boiling sulphur (440°).

Carbon dioxide	57·28
Carbon monoxide	42·72
	100·00

Experiment V.—Temperature of carbon 440°.

Carbon dioxide	60·86
Carbon monoxide	39·14
	100·00

Experiment VI.—At 440°.

Carbon dioxide	46·81
Carbon monoxide	53·19
	100·00

In the sixth experiment the rate of passage of the gas was increased to 40 bubbles a minute.

Experiment VII.—Instead of air a mixture of oxygen and nitrogen containing 15·4 per cent. of oxygen was used. It was contained in a large bell-jar dipping in a large and deep pneumatic trough (fig. 4). Temperature of the carbon 440°.

Percentage of carbon dioxide	=	33·4
„ carbon monoxide	=	66·5
		99·9

Thus carbon monoxide is always produced when carbon is heated in such mixtures of oxygen and nitrogen at temperatures below 500°. It might, however, be due to the reaction

$$CO_2 + C = 2CO$$

instead of

$$2C + O_2 = 2CO.$$
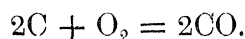
This supposition was proved to be untenable by the following experiments :—

Experiment I.—Pure carbon dioxide was passed very slowly over carbon heated to the melting-point of lead chloride (500°). The gas was then collected over mercury in a gas pipette. 278 c.c. of gas was collected in three hours, so that about 1·5 c.c. of gas passed over the charcoal in a minute. This collected gas was entirely absorbed by caustic potash.

Experiment II.—At the same temperature 150 c.c. of carbon dioxide was passed over the heated charcoal at the rate of 1 c.c. a minute. It was entirely absorbed by caustic potash.

Experiment III.—The carbon dioxide was passed over charcoal at 440°, the gas being afterwards passed through two sets of potash bulbs, over red-hot copper oxide, and through a third set of potash bulbs to analyse the gases produced. The first set gave an increase in weight of ·4548 gram, the second set no increase, and the third set no increase. The experiment lasted four hours. Therefore at these temperatures carbon dioxide is not decomposed by carbon, and the carbon monoxide in the former experiments must have been formed by direct union of carbon and oxygen.

The question now arises, Does the burning of carbon under ordinary circumstances take place in two stages? Is carbon monoxide first produced, and this by further oxidation transformed into the dioxide? The problem seems incapable of direct solution. I venture to advance the following considerations with regard to it :—

I. It has been proved by direct experiment that more carbon monoxide is burnt by air at 500° than at 440°. We find, in the results described above, that when carbon is burnt in air at 440°, more carbon monoxide appears in the products of combustion than at 500°, amounting in one case to 53 per cent.

II. It has been proved, also, that when the oxygen is diluted with a larger quantity of nitrogen than is contained in air, less carbon monoxide is oxidised, though the oxygen is present in excess. In the experiment already described, by diminishing the percentage of oxygen from 21 to 15, we get a larger quantity, 66 per cent., of carbon monoxide in the products of combustion.

III. Lastly, by drying the oxygen in which the carbon is heated, the percentage of carbon monoxide is largely increased, amounting in one case to 94·7 per cent. of the products of combustion.

And since it is found that, when the conditions of the experiment are made more and more unfavourable for the oxidation of carbon monoxide, (1) by lowering the temperature, (2) by decreasing the proportion of oxygen to nitrogen, (3) by drying the oxygen, we get more and more carbon monoxide produced, are we not justified in assuming that the combustion of carbon first produces this lower oxide?

Combustion of Sulphur in Oxygen.

In the preliminary experiments on the combustion of sulphur in dried oxygen, the sulphur used was purified by repeated sublimations.

Experiment I.—The sulphur was placed at one end of a tube filled with oxygen, phosphorus pentoxide being introduced at the other to dry the gas. The tube was sealed up and left drying for five days.

The tube was heated by an Argand burner, side by side with a similar tube containing sulphur in moist oxygen. The sulphur began to melt at the same moment in both tubes. Soon afterwards there was a sudden explosion in the moist tube, and a few seconds later a small blue flame appeared on the surface of the dry sulphur. This continued for a short time and was then extinguished. On analysing the gases in the two tubes, oxygen was found in the free state in the dry tube, but not in the moist tube.

Sulphur was then further purified as follows :—Some powdered sulphur was resublimed, and as it might contain hydrogen, or some compound of hydrogen, it was melted in a slow stream of sulphur chloride vapour, and distilled several times in an atmosphere of this substance. Some hydrochloric acid gas was produced, showing that this precaution was not needless. One end of the tube was sealed and the other bent and fixed into one neck of a dry WOULFF's bottle. The other neck was connected with a water pump which maintained a nearly complete vacuum in the apparatus. The sulphur was kept at a temperature of 150°–180° by an Argand burner. In this way all the sulphur chloride was got rid of.

Experiment II.—A tube was sealed up containing this purified sulphur in oxygen, and was left drying for five days as before. It was heated over an Argand lamp with a comparison tube containing some of the purified sulphur in moist oxygen.

The moist sulphur was seen to burn with a sudden flash, while the dry sulphur was distilled several times backwards and forwards in the tube without any visible combustion. Analysis of the contents of the dry tube showed that only $\frac{1}{12}$th of the oxygen had been converted into sulphur dioxide.

Combustion of Carbon Bisulphide in Oxygen.

The union of these two substances as brought about by an electric spark is well known to be extremely energetic. It seemed of interest to investigate whether dryness has the same effect on the burning of carbon bisulphide as it has on the burning of each of its constituents when heated separately in oxygen.

Purification of Carbon Bisulphide.—About 50 c.c. of the commercial substance were distilled five times from white wax, and in this way the liquid lost most of its unpleasant odour. To get rid of hydrogen compounds, as far as possible, it was sealed with a small quantity of chloride of sulphur in thick glass tubes and heated to 180° in an air bath for several days. The contents of the tube were distilled, the first portion only which distilled over at 46° being taken. This was shaken with pure mercury at intervals for several days until the metal remained bright after several hours' contact. The purified liquid was again distilled and sealed up with some phosphorus pentoxide. This drying agent seems to have no action on the bisulphide.

5 cubic centimetres of the vapour were collected over dried mercury, and to this vapour was added three times its volume of dried oxygen. A plug of phosphorus pentoxide was introduced, and the tube was left for twelve days. At the end of that time a spark of the smallest possible length from a small coil with one bichromate cell was passed through the mixture. The mixture exploded with a bright flash, leaving a deposit of sulphur on the sides of the tube.

A second experiment was tried in the same way, the mixture being allowed to dry for six weeks. The result was the same.

Two more experiments were made. Long tubes were carefully dried ; phosphorus

pentoxide was introduced at one end and sealed bulbs of purified carbon bisulphide at the other. A stream of dried oxygen was passed through the tubes and the ends sealed. The bulbs of carbon bisulphide were then broken, and the vapour, mixed with oxygen, was allowed to dry over phosphorus pentoxide for two weeks. Each tube was then heated over an Argand burner with a comparison tube containing the same gases in a moist state. Though the wet tubes exploded first in every case, the dry ones did so a few seconds later, and apparently with equal force.

Combustion of Ordinary Phosphorus in Oxygen.

Commercial stick phosphorus was melted under a solution of potassium bichromate in dilute sulphuric acid, dried and heated to 60° in a sealed tube with phosphorus trichloride. The tube was allowed to project some 15 centimetres out of the air bath, so that the sublimed phosphorus could condense in the cool part, but it was so inclined that any chloride which distilled over should run back into the heated part, which contained the melted phosphorus, mixed with phosphorus pentoxide. In three weeks the greater part of the phosphorus was deposited in the cold part of the tube. The iridescent crystals were melted and allowed to run into the cooler end of the tube, which was drawn out to a diameter of about 5 mm. This part was then sealed off.

The tube of purified phosphorus was placed with some phosphorus pentoxide in a tube of hard glass bent at right angles, and previously heated to redness. One end of this was connected with the stoppered neck of a Bunsen's gas pipette by a joint of dried india-rubber. The pipette contained oxygen which had been drying for eight days over phosphorus pentoxide. The tube was exhausted as completely as possible by a Sprengel pump with two fall tubes, and the end connected with the pump sealed. The tubulure at the bottom of the pipette was connected with a flexible india-rubber tube, dried as far as possible, which was connected with a reservoir of dried mercury. The mercury reservoir could be raised or lowered according as a high or low pressure was desired (fig. 5). After the whole apparatus had been allowed to stand for a week to allow the small residue of air in the vacuous tube to dry, the following experiment was carried on in a dark room. The oxygen was admitted to the vacuous tube, and the tube containing the phosphorus was broken. On the pressure being diminished, a very faint luminosity was seen on the phosphorus, which flickered for several hours, the interval between the extinguishing and the reappearance of the light being about a second and a half. This flickering was not due to variations of pressure caused by the shaking of the mercury in the reservoir, as the experiment was carried on in a cellar with a stone floor, on a solid wooden bench screwed to the ground. The tap was then turned off and the tube allowed to dry for three days more. At the end of this time the luminosity had disappeared, nor did it show itself though the pressure was varied in every possible way. The phosphorus was then melted by heating the tube with a spirit lamp, and still no luminosity appeared. It

was then heated until the phosphorus boiled. A faint glow appeared for an instant and then vanished.

Fig. 5.
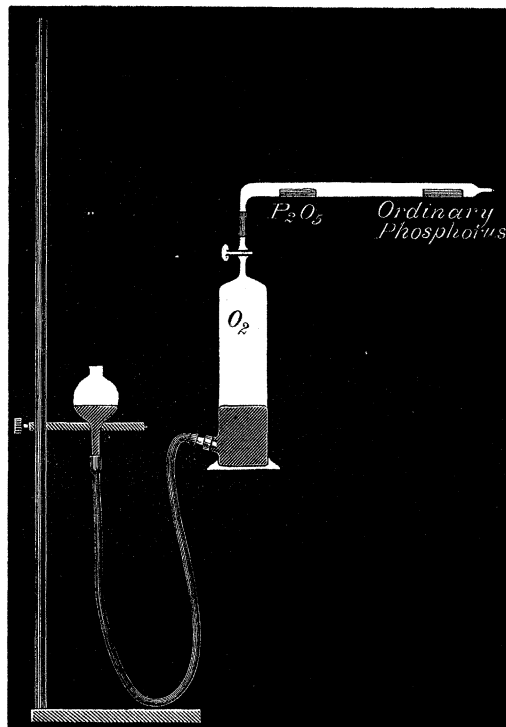
The india-rubber tube in connection with the pipette was then clamped. The phosphorus tube thus closed was removed from the pipette. The air was squeezed out of the free half-inch of india-rubber tubing, and a little water allowed to enter. Brilliant luminosity at once flashed out, and without any heating the phosphorus burst into a vivid white flame.

Ordinary phosphorus therefore does not burn in dry oxygen, though its temperature be raised to its boiling point (290°).

Combustion of Amorphous Phosphorus in Oxygen.

This substance was one of the first experimented upon, and, though it was by no means pure, it gave indications of a very different behaviour when heated in moist and in dry oxygen.

It was purified in the following way :—Commercial amorphous phosphorus was washed with water and dried by a current of air at 150° in a glass tube. One end of the tube was then sealed and the other connected with a mercury pump. The tube was exhausted and heated to 240°. A large quantity of gas was given off. No less than 75 c.c. were evolved from 5 grams of phosphorus. On allowing a bubble to escape into the air it caught fire. It had a strong smell of phosphine.

When no more gas was evolved, the tube was removed from the pump and sufficient phosphorus trichloride added to cover the phosphorus. The chloride was boiled and the tube sealed. It was heated in an air bath to 200° for three days. Any traces of phosphine or hydrogen would attack the chloride of phosphorus with formation of hydrochloric acid and free phosphorus. The tube was opened and the phosphorus chloride distilled off. To get rid of hydrochloric acid, the phosphorus was heated in a vacuous tube which had a piece of solid potash at the other end.

To get rid of any traces of ordinary phosphorus which might have been formed in these processes, a stream of purified air was drawn over the purified substance heated to 100° for two days.

Tubes were constructed like those used for carbon, with plugs of phosphorus pentoxide at one end and purified amorphous phosphorus at the other. These tubes were each heated over an Argand burner with a similar tube containing the same phosphorus in moist oxygen. In six of them, which had been drying from 2–5 weeks, no visible combustion could be observed, though the temperature was raised sufficiently high to distil the phosphorus. It condensed in yellow globules which could again be distilled, confirming the last results obtained on the influence of moisture on the combustion of ordinary phosphorus. After the experiments the gases were analysed, and found to consist of pure oxygen. In one experiment the tube had been standing for two months. The phosphorus pentoxide was very moist, and it was thought probable that the gas would not be sufficiently dry to prevent combustion. The end of the tube containing the phosphorus was heated over a $\frac{1}{2}$-inch flame of an Argand burner, side by side with a comparison tube of phosphorus in moist oxygen. In a little time the moist phosphorus burnt with a bright white light. The dry phosphorus began to distil slowly. When the heavy white vapour reached the moist oxide of phosphorus it burnt with a green flame quite slowly, the flame repeatedly going out and being re-kindled. The flame never moved to any other point, but burnt in this position until all the oxygen was used up.

These experiments show that phosphorus, both in the crystalline and the amorphous state, does not undergo combustion when heated in dry oxygen.

The Temperature required for the Combustion of Amorphous Phosphorus.

It was frequently noticed that amorphous phosphorus burnt readily at 360°, the boiling-point of mercury. In order to see if a lower temperature would suffice, the following experiment was performed:—In the horizontal part of a long tube, bent at right angles, a small quantity of pure amorphous phosphorus was placed. The vertical part of the tube was open, and dipped into a trough of mercury. After the tube had been filled with moist oxygen, the other end which contained the phosphorus was sealed. This end was inserted in the hole in the side of the air bath. The temperature was kept constant at 260°. After ten minutes the mercury had risen 5 centi-

metres in the tube. The combustion went on gradually, diminishing slowly in rapidity, and was complete in four hours. The presence of the phosphorus pentoxide produced tends to dry the gas, which would, I think, account for the diminution in the rate of combustion.

A similar experiment was made with moist oxygen at a temperature of 70°. No diminution in volume of the oxygen was noticed, though the tube was heated for three days continuously.

The temperature of the bath was raised to 100°, and kept constant for twenty-three days. During this long heating the combustion was proceeding very gradually, and at the end of the time half the oxygen was used up. The combustion of amorphous phosphorus, therefore, at 100° is very slow.

To show the difference which dryness makes in the rate of combustion, two similar tubes were heated to 100° in the same air bath. One contained phosphorus in oxygen which had been previously dried by a plug of phosphorus pentoxide for three days. The oxygen in the other was kept saturated with moisture by a drop of water floating on the mercury within the tube. After being heated to 100° for seven days both tubes were examined. In the dry tube the mercury had risen 8 mm.; in the wet tube it had risen 150 mm.

They were heated another seven days. The combustion in the wet tube was complete; in the dry tube the mercury had only risen 2 mm. In the former experiments, therefore, the phosphorus pentoxide produced does diminish the rate of combustion.

The luminosity of phosphorus is extinguished if a trace of turpentine vapour be present. A drop of turpentine was allowed to float on the surface of the mercury in a tube containing amorphous phosphorus in moist oxygen. It was heated to 100° as before. The combustion was perceptibly slower than before, though the oxygen was kept saturated with moisture. It went on gradually, however, until after seven days the mercury had risen 100 mm.

Amorphous phosphorus, as has been stated by many observers, undergoes an extremely slow combustion when allowed to stand in air. After having been kept for a year in a stoppered tube, a specimen of the pure substance was found to be quite moist, and, when it was washed with pure water, the washings gave the reactions of phosphoric acid.

The Conversion of Amorphous Phosphorus into Yellow Phosphorus.

In one experiment on the combustion of amorphous phosphorus in oxygen, I wished to be quite sure that the temperature to which the wet and dry tubes were heated was the same. Two such tubes were prepared, bent in the middle at a right angle. The phosphorus pentoxide in the dry tube was placed in one arm of the bent tube, the phosphorus being in the other. The ends of the two tubes containing the phosphorus

were passed through the cork of a large boiling tube containing mercury. A long tube open at both ends and passing through the cork served to condense the mercury vapour.

Fig. 6.
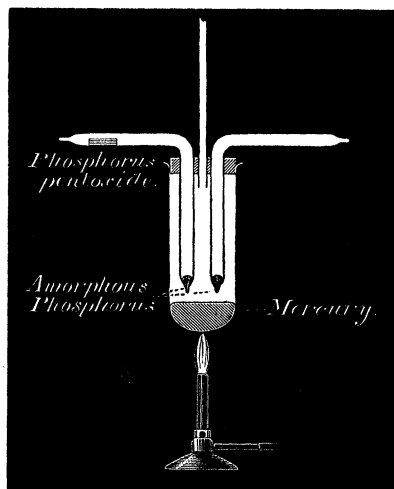
The mercury was boiled. After a few minutes the wet phosphorus burnt, the dry phosphorus showing no change. Further than that, though kept in the boiling mercury for four hours, it was apparently unaltered. We should have expected that it would have been, partly at all events, transformed into the ordinary modification. Is it possible that the change from one modification to the other is affected by dryness?

To answer this question the following experiment was undertaken:—Two tubes containing pure amorphous phosphorus in (a) moist and (b) dry nitrogen were heated in the vapour of boiling mercury for four hours. The phosphorus in both tubes was apparently unaltered. No sublimate of ordinary phosphorus could be seen on the cold parts of either tube. When the same tubes were heated in sulphur vapour at 440°, the production of ordinary phosphorus was quickly noticed in both tubes. Dryness does not apparently affect the temperature of the change.

Two tubes were prepared bent at right angles. A small quantity of amorphous phosphorus was placed in each, and one was filled with pure nitrogen, the other with pure oxygen, both gases being saturated with aqueous vapour. The ends of the tubes were then sealed. In order to heat the phosphorus contained in them, the limbs containing the phosphorus were placed in an air bath, holes being cut in its sides for their reception. The air bath was provided with a PAGE's regulator and the temperature was kept constant at 260°. The other limbs of the tubes were outside the air bath and were kept cool (fig. 7).

After six hours the tubes were removed. No perceptible change had taken place in the nitrogen tube; a small quantity of ordinary phosphorus appeared on the cold part of the oxygen tube.

When the tip of the oxygen tube was broken under mercury the liquid rushed in and filled the tube, showing that combustion was complete. The nitrogen tube was taken into a dark room, and the points of both ends broken. A current of air was drawn through it with the mouth. No taste or smell was perceptible, and after this treatment no luminosity appeared in the tube. A trace of ordinary phosphorus can be detected in this way. We must conclude, therefore, that at this temperature of 260° no change takes place when amorphous phosphorus is heated in a sealed tube containing nitrogen.

LEMOINE ('Deutsch. Chem. Gesell. Berichte,' 1867) has shown that the conversion of amorphous phosphorus into the ordinary modification is prevented if there is a considerable tension of phosphorus vapour in the tube. Though it was scarcely probable that this would exist in the tubes above described, where no taste of phosphorus was found in the gas, it was thought advisable to perform two experiments without sealing the tubes in which the phosphorus was heated. Nitrogen was

Fig. 7.
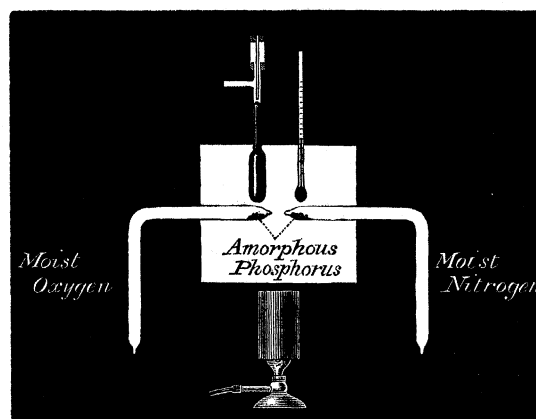
prepared in quantity by exposing the air in large bell-jars to the slow action of sticks of phosphorus. When the sticks were no longer luminous, the nitrogen was considered ready for use. In order that no vapour of phosphorus should accompany the nitrogen, the gas was passed through a tube containing red-hot copper oxide. It then bubbled through a solution of alkaline pyrogallate to take out the last traces of oxygen, and was then passed over pure amorphous phosphorus contained in a long tube. To prevent access of air a wash bottle of water was connected with the end of this tube. The tube itself passed through an air bath which was fitted with a PAGE'S regulator.

In the first experiment the air bath was kept constantly heated to 265° for three hours, a slow current of nitrogen being passed through the tube. No deposit of ordinary phosphorus was found on the cold part of the tube. In the second experiment the phosphorus was kept for five hours at a temperature of 278°, but not only was no deposit of phosphorus produced, but, after cooling, no smell or taste of ordinary phosphorus could be detected by drawing air through the tube. It is proved, then,

that amorphous phosphorus combines with oxygen at a lower temperature than that at which it is changed to the ordinary modification when heated in an inert gas. The statement which is ordinarily made that amorphous phosphorus, when heated to 260°, is converted into the yellow variety and if this is done in air or oxygen it then catches fire, is incorrect. Amorphous phosphorus must be considered as undergoing a true combustion, very slow at ordinary temperatures, slow at 100°, and quick at some temperature just below 260°.

Combustion of Tellurium in Oxygen.

The tellurium was purified by dissolving it in fuming sulphuric acid. The deep red solution was precipitated by the addition of water. It was thought that the possibility of occluded hydrogen being present would be obviated in this way. As has been shown, hydrogen has a great influence in bringing about combustion in dried gases, and its elimination was made a principal object in these purifications. The precipitated tellurium was washed with distilled water several times, and dried by heating in vacuo over phosphorus pentoxide.

It was placed in hard glass tubes in oxygen dried (1) for two, (2) for three weeks, but in both cases, when heated over an Argand burner with comparison tubes filled with moist oxygen, combustion appeared to take place with as much readiness as was the case when moisture was present.

Combustion of Selenium.

Selenium was purified by several sublimations, at first *in vacuo*, then in selenium chloride vapour. It was then freed from all traces of the chloride by repeated sublimations *in vacuo*, pieces of solid potash being present.

Tubes were prepared containing this purified selenium in pure oxygen. In some of them the oxygen was dried by phosphorus pentoxide, while in the others the oxygen was saturated with aqueous vapour.

Experiment I.—A tube containing selenium in oxygen, which had been standing in contact with phosphorus pentoxide for two weeks, was heated with a similar tube containing selenium in moist oxygen. The dry selenium began to burn at the same moment as the moist, with a slightly less intense flame. On analysis the oxygen was found to be totally used up in both tubes.

Experiment II.—The tube containing selenium in oxygen, dried by phosphorus pentoxide, was allowed to stand for two months. It was supported above an Argand burner with a tube containing selenium in moist oxygen. No difference could be observed between the combustion of the moist and dry substances.

Selenium, therefore, when purified in this way, burns in dry oxygen.

Combustion of Boron in Oxygen.

In these experiments the boron used was given to me by Mr. FRANCIS JONES, of Manchester. It had been prepared by him in his researches on boron hydride. As hydrogen might be occluded in the substance, it was heated in a tube of hard glass connected with a Sprengel pump. About twelve times its volume of gas was evolved, which burnt in air with a green flame. It was probably boron hydride. The boron was then sealed in a tube with oxygen, and left drying for a week. It burnt readily on heating. As all the hydrogen might not have been removed, it was placed in a tube, and heated for three days in an air bath at 200° in boron chloride vapour. A large quantity of hydrochloric acid was produced, and it was only after treating it in this manner three times that the boron chloride did not evolve hydrochloric acid gas. After the hydrogen had thus been eliminated, the boron was heated in dried oxygen, and found not to undergo combustion at the bright red heat of the blow-pipe flame. The end of the glass tube in this experiment was bent and made to dip under mercury, to prevent the glass from blowing out under the pressure of the heated oxygen.

Combustion of Arsenic in Oxygen.

Commercial arsenic was mixed with purified charcoal and heated in a vacuous glass tube. The crystalline sublimate was heated in a sealed tube with arsenic chloride vapour. The arsenic was then distilled again in a vacuous tube, at one end of which was a piece of solid potash to absorb hydrochloric acid.

Two experiments were made with this substance. In the first the oxygen was dried over phosphorus pentoxide for one, in the second for two months. The arsenic was found to burn as readily when dry as when moist, and when the ends of the tubes in which the experiments were done were broken under mercury, the mercury filled them entirely, showing that the oxygen was used up in both cases.

Arsenic, therefore, when purified in this way burns in dry oxygen.

Combustion of Antimony in Oxygen.

This element was prepared by heating tartar-emetic with charcoal. The metal so obtained was powdered, and placed in a hard glass tube, which was then filled with chlorine. The tube was then heated to 200° in an air bath. The process was repeated twice. The antimony so obtained was freed from hydrochloric acid by heating *in vacuo* over potash. On being heated in oxygen which had been dried for six weeks, it was found to burn readily. Two other experiments were done, in one of which the antimony was heated in oxygen which had been dried over phosphorus pentoxide for four months but neither showed any difference in behaviour between the moist and dry gas.

General Conclusions.

1. Pure charcoal, heated in oxygen dried by phosphorus pentoxide, does not burn with a flame. Partial combustion, however, goes on, both carbon monoxide and carbon dioxide being formed.

2. If the charcoal is mixed with platinum black, and heated in the same way in oxygen, about the same amount of charcoal is burnt. Carbon dioxide is, however, the only product.

3. When charcoal burns in oxygen, its combustion probably goes on in two stages. It forms, first, carbon monoxide, and, if circumstances are favourable, this undergoes further oxidation to the dioxide.

4. Sulphur, boron, amorphous and ordinary phosphorus do not burn in dried oxygen. Ordinary phosphorus does not even show luminosity, at any pressure, in dried oxygen.

5. Amorphous phosphorus is not converted into ordinary phosphorus when heated in nitrogen to 278° C. This substance undergoes true combustion when heated to 260° in moist air or oxygen, without any previous change to the crystalline variety.

6. Selenium, tellurium, arsenic, and antimony show no difference in their combustion, whether the oxygen be moist or dry.

I am indebted to Professor H. B. Dixon, F.R.S., for much valuable advice and encouragement during the progress of this investigation.