Third Liversidge Lecture.

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Fifty Years' Experimental Research upon the Influence of Steam on the Combustion of Carbonic Oxide.

INTRODUCTION.

WHEN the Council asked me to give the third Liversidge Lecture in the place of my revered master Professor Harold B. Dixon, whose sudden death on 18th September last removed a brilliant pioneer in combustion research, I decided to make it a review of the experimental work of the past fifty years arising out of his epoch-making discovery of the influence of moisture upon the combustion of carbonic oxide. For, as he was wont to say, " it loosed a hare which, though since pursued by the hounds in full cry, is still uncaptured."

In presenting the story I shall deal chiefly with the principal experimental discoveries interwoven with the various theories which have been advanced to explain them only so far as they are necessary to historic completeness. For the occasion is not one for the advocacy of any particular view; and therefore I shall endeavour to set forth the facts without bias, and to show some experiments illustrating them, leaving my hearers to draw their own conclusions. I am sure that this would be most consonant with Dixon's own wish; for, while impressing on all his pupils the paramount importance of the highest standard of experimental work, he attached little value to theories, save as working hypotheses.

My review may be conveniently divided into two parts, the first dealing with the period 1877 to 1900, when purely chemical theories were mainly under discussion, and the second with the physico-chemical aspects of the case, with which later work has chiefly been concerned.

PART I.

H. B. Dixon's Discovery (1877—1880).

It was in 1873, at the instance of the late Dr. A. Vernon Harcourt, that H. B. Dixon, who had gone up to Christ Church, Oxford, with a classical scholarship from Westminster School two years previously, turned his attention to science. And three years later, also at Harcourt's instigation, he began repeating R. W. Bunsen's experiments (1853) upon explosions of mixtures of electrolytic gas with increasing amounts of carbonic oxide, the results of which were regarded as inconsistent with the principle of mass action enunciated by Berthollet in 1805, and had led to the erroneous view that a continuous alteration in the composition of such a gaseous medium produces a discontinuous (" *per saltum* ") alteration in the course and products of its explosion (*Annalen*, 1853, **85**, 137 ; Bunsen, " Gasometrische Methoden ").

In the year 1877, while repeating Bunsen's work, Dixon happened to pass a series of sparks through a $2CO + O_2$ mixture at 300 mm. pressure contained in a eudiometer over mercury, where it had been for some time in contact with pieces of solid caustic potash. To his surprise, however, no explosion resulted, even when the experiment was repeated. Thinking that possibly something might have been wrong with the carbonic oxide, which had been prepared from magnesium formate, he repeated the experiment once more, using carbonic oxide of a different origin, but with the same result. As it then occurred to him that the only unusual condition had been the dryness of the medium, he added a little water vapour to it, when, on again passing a spark, an explosion instantly resulted.

On pursuing the matter further, using henceforth phosphoric anhydride as his drying agent, he made many experiments proving that a $2CO + O_2$ mixture which had been dried by contact with it for several days can be subjected at atmospheric pressure to a series of sparks from a Ruhmkorff coil without exploding, although the addition of a minute trace of steam at once rendered it explosive.

This momentous discovery was first announced by Dixon in a paper to Section B of the British Association Meeting at Swansea on 26th August, 1880 (*B.A. Reports*, 1880, p. 503), on which occasion he demonstrated it by three experiments, the first two of which will be repeated before you.

In the first experiment, sparks were passed across a gap of about 1 mm. between platinum wires, through an 8-days phosphoric anhydride-dried $2CO + O_2$ medium sealed up at atmospheric pressure in a horizontal glass tube (Fig. 1*a*)* without any explosion resulting. In the second experiment, no explosion occurred when sparks were passed through a similarly dried medium at atmospheric pressure contained in a vertical glass tube (Fig. 1*b*) sealed at the lower but closed at the upper end by a stop-cock ; but on admitting a drop of water through the stop-cock, and re-sparking a few minutes later, an explosion instantly resulted. In the third experiment, no explosion occurred on sparking a similarly dried medium sealed up at atmospheric pressure in a vertical glass tube (Fig. 1*c*) having a

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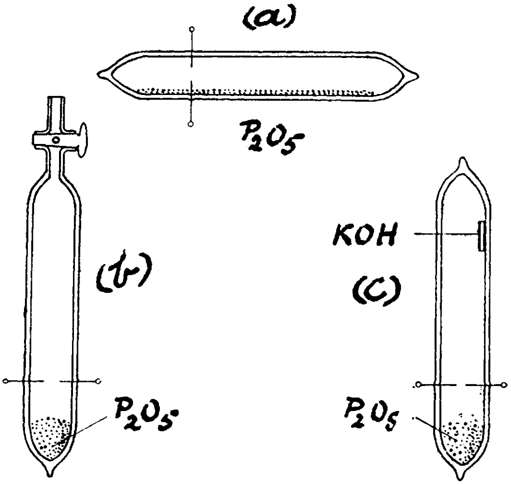
* With the exception of Figs. 1, 2, and 3, the illustrations are reprinted by permission from the *Philosophical Transactions* and the *Proceedings* of the Royal Society.

small piece of solid caustic potash fused on to the upper part of its inner surface; but on gently heating the potash by means of a flame from without (whereby a minute amount of moisture would be liberated from it) and then re-sparking the medium, it exploded instantly. (The first and second experiments were successfully repeated on the lecture table.)

FIG. 1.



H. B. Dixon's Further Experiments (1880—1893).*

Dixon next endeavoured to find whether the steam had acted chemically, or merely as a " third body." This he did by sparking a series of phosphoric anhydride-dried $2CO + O_2$ mixtures to which about 1% of various foreign gases, similarly dried, had been added beforehand. It was thus found that, whereas any and all hydrogen-containing substances would render such a medium explosive, no other sort was effective. Thus he found that:

Whereas	HCl CH_4	were	both	effective,	CCl_4	was not.
"	CH_4 NH_3	"	"	"	C_2N_2	"
"	NH_3 H_2O	"	"	"	NO	"
"	H_2O H_2S	"	"	"	SO_2	"
"	H_2S C_2H_4	"	"	"	CS_2	"

Hence, he concluded, the explosibility of a carbon monoxide–oxygen medium is conditioned by the presence of some hydrogen-containing

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* *Phil. Trans.*, 1884, **175**, 617; 1893, **184**, 97.

gas or vapour capable of generating steam, whose function it is to act as a "carrier" of oxygen to the carbonic oxide (*B.A. Reports, loc. cit.*), thus:

$$\left\{\begin{array}{ll}\text{(i)} & CO + OH_2 = CO_2 + H_2 \\ \text{(ii)} & 2H_2 + O_2 = 2H_2O\end{array}\right\}$$

In another series of experiments, made during 1880—1884, he compared the average rates of flame propagation between two points about a metre apart in a brass tube of 13 mm. internal diameter filled at atmospheric pressure with a $2CO + O_2$ mixture in different hygroscopic states between "well-dried" and "saturated with water vapour at 35°," the speed measurements all being made at the last-named temperature. These showed that the mean flame-speed rapidly increased with the moisture-content of the medium, thus:

$2CO + O_2$ Medium.	Moisture, %.	Mean flame speed, metres per sec.
Dried by passage over fresh P_2O_5	—	44
,, ,, ,, previously used P_2O_5 ...	—	69
,, ,, through conc. H_2SO_4	—	103
Saturated with moisture at 6° C.	0·9	125
,, ,, ,, 8	1·06	155
,, ,, ,, 12	1·34	200
,, ,, ,, 35	5·5	226

Subsequently, in his Bakerian Lecture to the Royal Society in 1893 upon "The Rate of Explosion in Gases," he published the following rates of detonation for $2CO + O_2$ mixtures in different hygroscopic states:

$2CO + O_2$ Medium.	Moisture, %.	Rate of detonation, metres per sec.
Well dried by conc. $H_2SO_4 + P_2O_5$	—	1264
Dried by conc. H_2SO_4 only	—	1305
Saturated with moisture at 10°	1·2	1676
,, ,, ,, 20	2·3	1703
,, ,, ,, 28	3·7	1713
,, ,, ,, 35	5·6	1738
,, ,, ,, 45	9·5	1693
,, ,, ,, 65	24·9	1526
,, ,, ,, 75	38·4	1266

It was thus shown, what has since been confirmed by other investigators, that, both *before* and *after* detonation has been set up, the flame-speed in a $2CO + O_2$ explosion increases with its moisture content up to a maximum with about 5·6% thereof, any more of it merely acting as a diluent; this important fact should always be remembered when theories about the function of steam are being discussed.

The slowing down of the flame speed on removal of moisture from such a medium will now be illustrated by an experiment in which the rapid flame speed set up on igniting a "moist" 20%CO/80%air medium in a long horizontal tube may be contrasted with the much slower speed similarly set up in the same medium after it has been dried by passage through 80% sulphuric acid, and with its non-ignitibility by a taper when it had been still further dried by means of 98% sulphuric acid.

H. B. Baker's Discoveries (1883—1902).*

Excepting those on "rates of detonation," all the experiments so far mentioned had been made during the ten years (1877—1886) of Dixon's Oxford research period, when for a while (1883—1884) H. B. Baker had collaborated with him ; and to complete this part of the review, reference must be made to Baker's discoveries, and especially those concerning the oxidation of carbon. Working, first of all in Dixon's laboratory at Balliol College, Oxford, and afterwards independently at Dulwich College, London, he found that, when heated to redness in carefully dried oxygen, highly purified charcoal burns very slowly without any visible flame principally to the monoxide, the proportion (always very small) of dioxide formed varying inversely with the dryness of the system. Thus, for example, whereas after one week's phosphoric anhydride-drying, the products resulting from the slow passage of oxygen over the strongly heated charcoal contained CO_2, 5·0; CO, 40·0; and O_2, 55%, after two weeks' drying they contained CO_2, 1·7—2·0; CO, 27·8—39·5; and O_2, 58·1—70·5%.

Moreover when, in 1884, Baker showed that highly purified dry sulphur and phosphorus even can be repeatedly distilled backwards and forwards in a glass tube containing phosphoric anhydride-dried oxygen at atmospheric pressure without any combustion whatever occurring, although the admission of even a trace of moisture instantly causes a vivid burning, chemists realised that moisture functions generally, if not universally, in promoting combustion. Finally, in 1902, Baker crowned these remarkable achievements by showing that highly purified and carefully dried electrolytic gas is quite unreactive at temperatures (dull red heat) where the undried medium readily explodes—a result which G. W. Andrew and myself had no difficulty in confirming at a temperature of 525°, save that in our case the moist medium combined non-explosively. Baker also observed that, in one experiment out of twenty, an "extremely small spark" could be passed through phosphoric anhydride-dried electrolytic gas without causing an explosion.

Some Essential Precautions.—Needless to say, such results aroused universal interest, and many attempts were made to repeat them,

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* J., 1885, **47**, 349; 1902, **81**, 400; *Phil. Trans.*, 1888, **178**, 571.

some of which failed owing to neglect of certain essential precautions, the importance of which cannot be over-rated. To describe them fully would take up many pages, and as the more important of them were dealt with in papers recently communicated to the Society by H. B. Baker and myself (J., 1929, 1601, 1604), it will suffice here to say that principally they comprise (i) extreme cleanliness, especially in regard to all the inner surfaces of containing vessels, (ii) extreme purification of each and all the various gases and materials used, (iii) total avoidance both of organic lubricants on stop-cocks and of rubber joints, in the apparatus, (iv) the use, as final drying agent, of redistilled and purified phosphoric anhydride quite free from lower oxides, a requirement first shown by Shenstone about 1890—1893, and (v) the employment of explosion or reaction vessels made out of some special quality of glass as non-retentive of moisture as possible.

Personally, in experiments where the most intensive drying is arrived at, I avoid altogether using either calcium chloride or sulphuric acid as a " pre-drier," and use only solid caustic potash (but *not* " purified by alcohol ") and spirals immersed in liquid air before applying my final drier; this is always redistilled and purified phosphoric anhydride which should be as white and powdery as is virgin snow below zero.

The Drying Power of Phosphoric Anhydride.—As to the drying power of the redistilled and purified phosphoric anhydride used in such experiments, as long ago as 1887 E. W. Morley made careful measurements, extending over several months, of the moisture content of air which had been passed at the rate of 3 litres per hour (i) over " moistened calcium chloride," and (ii) through a glass tube, 8 cm. long and 2 cm. internal diameter, filled with pure redistilled phosphoric anhydride, finding it thereby reduced to as little as 1 milligram in 40,000 litres, or *circa* 1 in 32 million by volume. On repeating the experiment in 1904, he concluded that what he had formerly supposed to be residual water vapour was much more probably phosphoric anhydride vapour, and that the drying of a gas by even such short contact with such phosphoric anhydride may be considered as virtually absolute (*Amer. J. Sci.*, 1887, **34**, 199; *J. Amer. Chem. Soc.*, 1904, **26**, 1171).

Clearly then, the prolonged drying period required in experiments in which " intensive drying " is arrived at does not arise from any difficulty in drying the gaseous medium itself by means of phosphoric anhydride, but from that of getting rid of the last trace of moisture obstinately adhering to the walls of the containing vessel. To ensure this, periodically during the drying period the walls should be heated to 150—200°, care being taken to keep cold the part of the vessel where the phosphoric anhydride is. When such means are adopted, a drying period of 250 days suffices to dry to the extreme possible limit a gaseous medium which is sealed up in contact with pure redistilled phosphoric anhydride in a hard-glass vessel of about 100 c.c. capacity.

M. Traube, Mendeléeff, and H. E. Armstrong (1885—1892).

Among the first of many workers which Dixon's discovery brought into the field was M. Traube, who in 1885 devised the familiar lecture experiment, which will now be repeated before you, showing the extinction of the flame of sulphuric acid-dried carbonic oxide by similarly dried air at atmospheric pressure. It may be recalled, however, that such a flame is not extinguished by sulphuric acid-dried oxygen.

Traube also proved the formation of hydrogen peroxide when a flame of either hydrogen or carbonic oxide is projected on to a surface of cold water or ice. We will now catch the water formed when a carbon monoxide blowpipe-flame is played upon a block of ice, and then (by testing it with both acid titanic sulphate and starch *plus* potassium iodide solutions) prove that it contains peroxide.

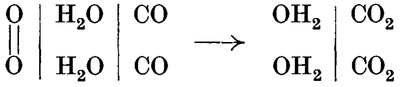
Traube (*Ber.*, 1885, **18**, 1890), however, went further and, claiming to have disproved the occurrence at high temperature of the $CO + OH_2 = CO_2 + H_2$ reaction postulated by Dixon, concluded that steam assists the combustion of carbonic oxide by conditioning the following reaction cycle—in which hydrogen peroxide functions essentially :

$$\left\{\begin{array}{ll}\text{(i)} & CO + O{:}O + OH_2 = CO_2 + H_2O_2 \\ \text{(ii)} & H_2O_2 + CO = H_2O + CO_2\end{array}\right\}$$

In 1886 Dixon dealt rather severely with this theory, refuting the error into which Traube had fallen in supposing the non-occurrence of the reduction of steam by carbonic oxide in flames (J., 1886, **49**, 106). In 1891, however, Mendeléeff, although rejecting Traube's first equation, supported his contention as to the intervention of hydrogen peroxide, as well as that of Dixon in regard to the rôle of steam, maintaining that, "*since reactions of equal volumes precede all others*," the following cycle of bimolecular reactions is probably needed for the combustion of carbonic oxide ("Principles of Chemistry," 1891) :

$$\begin{array}{ll}\text{(i)} & CO + OH_2 = CO_2 + H_2 \\ \text{(ii)} & H_2 + O_2 = H_2O_2 \\ \text{(iii)} & H_2O_2 + CO = CO_2 + H_2O\end{array}$$

In 1885—1886 H. E. Armstrong joined battle (Pres. Address, Chemical Section, Brit. Assoc., 1885; *Proc. Roy. Soc.*, 1886, **40**, 287; J., 1886, **49**, 112), challenging all concerned with the declaration that two perfectly pure substances are quite incapable of reacting chemically, but require the presence of an electrolyte to form a closed conducting circuit. In the case under discussion "conducting water" (*i.e.*, water associated with traces of impurity derived from the walls of the containing vessel) was supposed to be the requisite electrolyte, the oxygen playing the part of depolariser, thus:



$$\begin{array}{c|c|c} O & H_2O & CO \\ \| & & \\ O & H_2O & CO \end{array} \longrightarrow \begin{array}{c|c} OH_2 & CO_2 \\ & \\ OH_2 & CO_2 \end{array}$$

Before. After.

All these opposing views led to lively controversies during the "'nineties," and especially between Dixon and Armstrong, who never were able to compose their differences. Armstrong always insisted upon the fundamental *necessity* of his view, while Dixon always regarded as kinetically improbable a theory requiring the simultaneous collision of as many as five molecules. Their contention, however, greatly stimulated interest on the subject, and has caused many important experiments to be made which otherwise might not have been undertaken. Notwithstanding all these, as recently as 1925 Armstrong still declared carbonic oxide to be "*per se* an incombustible gas," putting forward a still more elaborate explanation of the essential function of steam (*Proc. Roy. Soc.*, 1925, *B*, **98**, 202).

To Mendeléeff's theory Dixon opposed the fact that, although there is no difficulty in exploding an undried equimolecular mixture of carbonic oxide and nitrous oxide, intensive drying renders it non-explosive when sparked. According to Mendeléeff, however, such an intensively dried mixture should have no difficulty in reacting, since equal volumes of its two constituents are both concerned and present. And to this no reply was made.

The Cyanogen Evidence and "Nascent Oxygen" Theory (1886—1896).

While the discussions referred to were proceeding, there arose in the "'nineties" another body of evidence out of researches upon the combustion of cyanogen, the import of which must now be considered.

Seeing that cyanogen is one of the most endothermic of gases—according to Berthelot, its molecular heat of formation is − 77 as compared with − 47 kg.-cals. for that of acetylene—and that the carbon which it contains burns in two well-defined stages, namely, first to the nonoxide and then to the dioxide, the study of its combustion is bound up intimately with that of carbonic oxide. As far back as 1886 Dixon (J., **49**, 384) had observed that in the explosion of cyanogen with an excess of oxygen the formation of carbonic acid is complete and unaffected by the presence of moisture; but at that time the full significance of such an observation was hardly recognised, because it was not until 1892 that Dixon proved that in the explosion wave a cyanogen–oxygen detonating mixture burns in two stages, thus (*Phil. Trans.*, 1893, **183**, 116):

$$\left\{\begin{array}{ll}\text{(i) \textit{In the wave-front} ....} & C_2N_2 + O_2 + O_2 = 2CO + O_2 + N_2 \\ \text{(ii) \textit{Behind it} ....} & 2CO + O_2 + N_2 = 2CO_2 + N_2\end{array}\right\}$$

When, in 1894, Smithells and Dent demonstrated the same two-stage combustion by analysing the interconal gases from an ordinary aërated cyanogen flame burning at atmospheric pressure in a Smithells flame separator, the proof that carbonic oxide is always the initial product was complete. And as the nascent carbonic oxide so produced is presumably at an extraordinarily high temperature, the possibility of its further combustion to the dioxide proceeding without the aid of steam became a live issue.

In 1890 Beketoff (*Bull. Acad. St. Petersburg*, No. 5, **2**, 175) had shown that a phosphoric anhydride-dried $2CO + O_2$ mixture becomes explosive by adding to it about 10% of similarly dried cyanogen, and had concluded that the combustion of carbonic oxide is conditioned by a supply of atomic oxygen which becomes available at the higher flame temperature caused by the addition of cyanogen to the burning medium. Moreover, he argued, steam promotes the combustion of carbonic oxide because it yields the requisite oxygen atoms more readily (*i.e.*, at a lower temperature) than does molecular oxygen which is stable (he said) at 2000°.

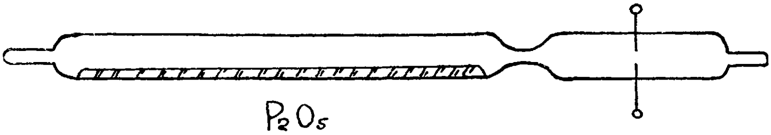
Although at the time Dixon seems to have been more impressed by this view than by any other as an alternative to his own, he said that, even if true, it only put off the difficulty one stage; for, he asked, "if carbonic oxide has not the power to break up oxygen, why should the liberated hydrogen do so?", adding that since the heat of formation of carbonic anhydride from carbonic oxide is greater than that of steam from hydrogen, "M. Beketoff only leaves us with a greater difficulty to explain." Nevertheless he made several experiments to test the "nascent oxygen" theory without finding any support for it.

First of all, he blended 7-days phosphoric anhydride-dried $2CO + O_2$ and $C_2N_2 + 2O_2$ mixtures in the ratios 4 : 1 and 2 : 1, respectively, so as to obtain the two-following composite media:

	(1) Per cent.	(2) Per cent.
CO	53·3	43·3
C_2N_2	6·7	11·7
O_2	40·0	45·0
	100·0	100·0

On sparking them, explosion resulted in each case with complete combustion of all the cyanogen *plus* two-thirds of the carbonic oxide in (1) and 87% of it in (2). So far, then, Beketoff's observation, though not necessarily his conclusion, was confirmed, the proportion of the carbonic oxide burnt increasing with the intensity of the exciting flame. Incidentally, also, these experiments vouch for the freedom of Dixon's cyanogen from hydrogen cyanide; for otherwise the combustion of the carbonic oxide would certainly have been complete in each case.*

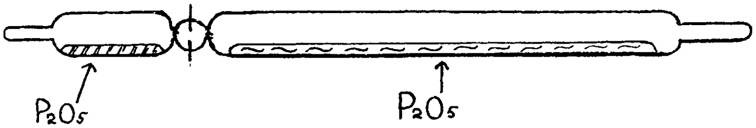
FIG. 2.



He next made a mixture of carbonic oxide and ozonised oxygen containing $36CO + 8O_3 + 56O_2$, and after drying it over phosphoric anhydride for a week in the tube shown in Fig. 2, he sparked it between platinum wires 7 mm. apart without any explosion resulting, although " there was a considerable halo of blue light in the path of the spark." Such result he regarded as unfavourable to the " nascent oxygen " theory, though perhaps not conclusive against it.

Much stronger rebutting evidence, however, was forthcoming from a singularly bold experiment made by Dixon in conjunction with E. J. (now Sir John) Russell in 1897 (J., **71**, 601). After sealing up over phosphoric anhydride a well-dried mixture of carbonic oxide, chlorine peroxide, and oxygen, in the volumetric ratio 60 : 29 : 11, in the glass tube shown in Fig. 3, and then allowing a 15-days drying-period, they eventually sparked it between platinum wires, whereupon " a blue flame traversed the tube and lingered some time at the end of the tube," so that there could be no doubt about the medium having been thoroughly inflamed. Yet subsequent analyses of the residual gas showed that, although there had been more than sufficient chlorine peroxide present to consume the

FIG. 3.



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* He always prepared his cyanogen by heating recrystallised and carefully dried mercuric cyanide, and usually passed the gas evolved through tubes packed with solid caustic potash.

whole of the carbonic oxide, no less than 76% of it remained unburnt. Dixon always regarded this result as well-nigh conclusive against Beketoff's theory, because it did not show "that oxygen just liberated from a compound is more active than ordinary oxygen in attacking carbonic oxide at a high temperature."

To return, however, to the burning of cyanogen, we will now show an experiment which was first made by Smithells and Dent in 1894 (J., **65**, 603). Into the bottom of a silica glass "flame separator," kindly lent me for the occasion by Professor Smithells, slow streams of (*a*) cyanogen from a gas holder over mercury and (*b*) air are being separately led, each through a long "drying-tube" packed with phosphoric anhydride. The two streams, mingling as they ascend the apparatus, issue as a homogeneous mixture at the orifice of the outer tube where, on applying a light, the two-coned aërated cyanogen flame is obtained. You will observe the beautiful lilac colour of the inner cone, in which the cyanogen is burning to carbonic oxide and nitrogen, that of the outer cone being the more familiar blue-green characteristic of burning carbonic oxide. Separation of the two cones first occurs when the C_2N_2 : air ratio is about 1 : 3·3. By suitable manipulation we will now detach the inner from the outer cone and draw it down until the two are separated by a vertical distance of about 4 or 5 inches. On our gently lowering a jar of sulphuric acid-dried air over the outer cone, it will be observed that its blue flame is immediately extinguished. When, however, by another manipulation we about halve the distance between the two cones and repeat the trial, it will be observed that the outer cone is no longer extinguished by, but continues to burn quite easily in, the sulphuric acid-dried air.

Such a result, which merely repeats what Smithells and Dent first observed in 1894, suggests that carbonic oxide, *when freshly liberated from a cyanogen flame*, has, and retains for a very short while, the power of combining directly with oxygen.

Two years later, this inference was reinforced by some comparative measurements by Dixon in conjunction with E. H. Strange and E. Graham of the duration of flame in detonations of "wet" and "dry" $C_2N_2 + 2O_2$ mixtures, respectively (J., 1896, **69**, 773). Two similar "detonation tubes," furnished at the same appropriate distances from the firing piece with glass windows of like dimensions, were fixed vertically side by side. After one of them had been thoroughly dried out, it was filled at atmospheric pressure with a $C_2N_2 + 2O_2$ mixture which had been dried for some days over phosphoric anhydride. The other tube was then similarly filled with the same mixture which had been saturated with steam at about 13° ($H_2O = 1·5\%$). The two mixtures were then fired simultaneously, and on reaching the windows the explosion flames were photographed on the same vertically moving film. To Dixon's surprise, with both slow and high film velocities, the two images were drawn out equally, which (he said) could only mean that "in a mixture of freshly formed carbonic oxide and oxygen, the gases unite as the mass cools down without the intervention of steam; and where steam is present, it does not appreciably alter the time during which the change continues."

The conclusiveness of such an experiment depends (as he was fully aware) upon the freedom of the cyanogen used from hydrogen cyanide; but the care which Dixon always bestowed on the purity of his gases, and particularly the results of his $CO–C_2N_2–O_2$ experiments already referred to, leave little or no room for doubt thereon, and certainly he himself had none.

Taken as a whole, and in conjunction with Dixon's other cognate experiments on this aspect of the case, the cyanogen evidence, so far from supporting Beketoff's "atomic oxygen" theory, favoured the view that the direct oxidation of carbonic oxide can be conditioned by a prior "excitation" of its molecules, in which state presumably they are born in a cyanogen flame. And such conclusion does not seem to be affected by the observation recently made in W. E. Garner's laboratory of there being a "distinct difference" between the total radiation emitted during the explosion of a "wet" and "dry" $C_2N_2 + 2O_2$ mixture (*Nature*, 1930, **125**, 705).

PART II.

Physico-chemical Experiments.

Although up to the end of last century interest had been chiefly centred round chemical aspects of the phenomenon, there were always people more inclined towards a physical explanation of it, especially when it became known that moisture promotes, not only other cases of combustion, but also many reactions where oxidation is not involved.

Lothar Meyer on Possible Influence of Temperature (1886).

As far back as 1886 Lothar Meyer (*Ber.*, **19**, 1099), in repeating some of Dixon's experiments, had found that a 6-days phosphoric anhydride-dried $2CO + O_2$ mixture, which did not explode when sparked in a eudiometer at 156 mm., could be made to combine non-explosively at the same pressure merely by passing a series of powerful sparks through it continually for about two minutes, combustion being complete. From this, he argued, the combustion of "dry" carbonic oxide appeared to be a matter of temperature only, a higher degree being required to initiate the *direct* than the *indirect* (*i.e.*, by steam) oxidation. To which Dixon replied by showing that the pre-heating of sulphuric acid-dried carbonic oxide did not enable its flame to continue burning in similarly-dried air, though such an experiment hardly seems conclusive on the point.

Experiments on the Effects of Ionisation (1893—1904).

In 1893 J. J. Thomson made the highly significant discovery that the intensive drying of a gas renders it electrically non-conductive even under considerable potential differences; and he pointed out that, since the forces holding the atoms together in a molecule are electrical, the presence in a gaseous medium of drops of liquid of high specific inductive capacity, such as water, would probably cause a sufficient loosening of the bonds between the atoms to render its molecules more reactive. Moreover, in a discussion upon the subject at the British Association (Sheffield) Meeting in 1910 (*B.A. Reports*, p. 501) he reminded chemists " that combustion was concerned not only with atoms and molecules but also with electrons, *i.e.*, bodies of smaller dimensions and moving with very high velocities. These may precede the explosion-wave and prepare the way for it by ionising the gas." As early as 1894, Braun (*Z. physikal. Chem.*, **13**, 155) had shown that there is " ionisation " in the explosion wave, doubtless due to the combined influence of very high temperature and chemical interactions. Also G. S. Turpin, working in Dixon's laboratory, had shown that the flame of an explosion wave in electrolytic gas remains conducting for about 0·001 sec. or almost as long as the duration of its luminosity ("Studies from the Physical and Chemical Laboratories, Owens College, I," 1893, p. 294).

Dixon, while urging the difficulty of supposing the presence of drops of liquid water in explosion flames—*e.g.*, in the detonation flame of a $2CO + O_2$ mixture containing an amount of moisture far below saturation at ordinary temperatures, the temperature of which has never been estimated below 3000°—always maintained an open mind to such explanation. Albeit, in 1896, both he and independently H. B. Baker (J., **69**, 789, 1308) had tried subjecting a well-dried $2CO + O_2$ medium to Röntgen rays while passing electric sparks through it, but without any inflammation resulting. Moreover, in 1914, in conjunction with C. Campbell and W. E. Slater, Dixon (*Proc. Roy. Soc.*, *A*, **90**, 506) failed to obtain any evidence of the detonation of either " moist " or " dry " $2CO + O_2$ mixtures being affected by strong magnetic fields (up to 10,000 gauss). Such negative results, however, can scarcely be regarded as decisive; and it is highly desirable that the experiments should be repeated with the much stronger " ionising " means and magnetic fields now available.

In his Wilde Lecture to the Manchester Literary and Philosophical Society upon " The Influence of Moisture in Chemical Changes in Gases " in 1909, H. B. Baker described experiments which had led him to the view that " ionisation without water is ineffective in producing chemical action," the co-operation of both " ions " and water vapour being necessary (*Mem. Manchester Phil. Soc.*, 1909, **53**, No. 16, 7).

The Ignitibilities of Dried $2CO + O_2$ *Media.*

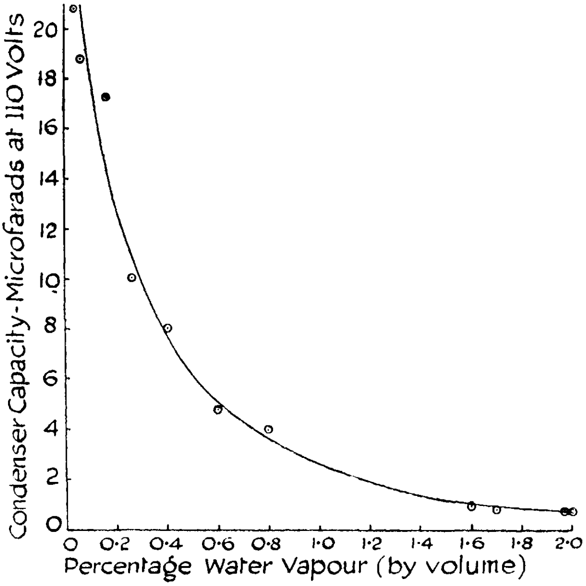
Apparently not until 1903 was any attempt made to correlate " degrees of dryness " and " ignitibilities " of a $2CO + O_2$ medium in different hygroscopic states. In that year, however, A. F. Girvan communicated a paper to this Society (P., **19**, 230) reporting that whereas a series of " powerful sparks " from an induction coil had failed to ignite such a medium after it had been dried by reducing its temperature below – 80°, ignition always resulted when the " drying temperature " had been between – 50° and – 35° only, while a single spark always caused an explosion if it had been – 15° only. He also observed that the resulting explosions with the medium dried at – 35° to – 50°, were always much slower and milder than with the moist gases.

When, in 1914—1916, W. M. Thornton's remarkable experiments on the electrical ignition of explosive gaseous media (*Proc. Roy. Soc.*, *A*, **90**, 272; **91**, 17; **92**, 9, 381) had definitely proved that, for given sparking conditions (*e.g.*, electrodes, type of discharge, voltage, etc.), a certain " minimum igniting current " is always required to ignite a particular mixture under given conditions of temperature and pressure—for example, a minimum capacity of *circa* 2 microfarads for a condenser discharge at 100 volts to ignite a " moist " theoretical carbon monoxide–air mixture at room temperature and pressure—the question naturally arose whether the non ignitibilities of rigidly dried carbon monoxide–oxygen mixtures might after all be only a matter of powerful enough sparks, especially as in Dixon's earlier experiments induction-coil sparks of quite moderate intensities only had been employed. Although I had often discussed this possibility with him, the opportunity of properly testing it experimentally did not come until after the War, when means were found in my laboratories at South Kensington. I will now describe some of the more outstanding results of our experiments, with which Dixon kept closely in touch right up to his death, being actually present when the more critical of them were made or repeated.

The Imperial College Experiments (1920—1930).

(1) *Effects of Progressive and Intensive Drying upon the Electrical Ignition of* $2CO + O_2$ *Mixtures.*—(*a*) In conjunction with Dr. F. R. Weston (*Proc. Roy. Soc.*, 1926, *A*, **110**, 614), determinations were made of the effects of progressive drying of a $2CO + O_2$ medium from " saturation at room temperature " down to " calcium chloride dryness " upon the minimum capacity required for its ignition by a discharge across platinum poles from a condenser charged up to 110 volts. The results, which lay on the hyperbolic curve reproduced in Fig. 4, showed a rapid increase on such minimum capacity as the drying progressed, until with calcium chloride dryness (H_2O = *circa* 0·03%) it became nearly thirty-fold that required with " saturation at 17·4° " (H_2O = 2·0%).

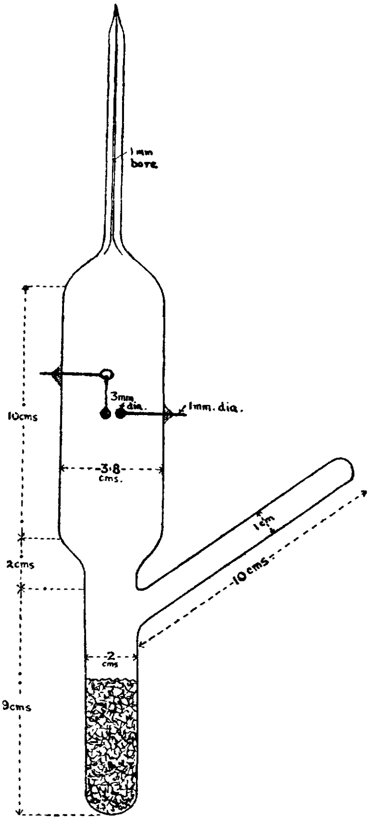
FIG. 4.



In considering such experiments, it should be remembered that a condenser discharge is oscillatory and characterised by extreme rapidity, the frequency being something like a million per second; it starts with collision-ionisation of the gas between the poles, which is at a maximum in the first oscillation; it also has a high temperature, and causes high local gas pressure, as is evident from the crackly sound emitted. Its incendivity depends on the character of the first oscillation, which is determined by the frequency and damping associated with the circuit employed.

(*b*) The next step was to determine whether a $2CO + O_2$ mixture which had been dried to the extreme limit possible by phosphoric anhydride could still be exploded if a sufficiently powerful condenser discharge-spark were used for ignition. Accordingly, highly purified $2CO + O_2$ media, after being subjected to a thorough preliminary drying *en route*, were sealed up under all due precautions at atmospheric pressure over pure redistilled phosphoric anhydride in cylindrical glass bulbs of about 100 c.c. capacity fitted with "balled" platinum electrodes, as shown in Fig. 5. The inner surfaces of the bulbs had been previously thoroughly cleaned, and the platinum electrodes glowed out for 20 hours, both *in vacuo* and in oxygen at 2—3 mm. pressure, so as to ensure elimination of organic matter and hydrogen from the system.

Fig. 5.



Altogether ten such bulbs (in three series) were so prepared and filled (*ibid.*, p. 615; 1929, *A*, **123**, 285), the subsequent "drying-periods" varying from 150 to 1000 days, during the whole of which the gaseous medium was in contact with the phosphoric anhydride; also, once a fortnight the body of each bulb was heated externally to about 200°, to ensure the dispersion of any adsorbed moisture film on its inner surface, the lower part containing the drying agent being specially cooled throughout the operation. There could be no doubt whatever about the extreme desiccation so effected, which would reach its utmost limit certainly after 250 days, and probably sooner.

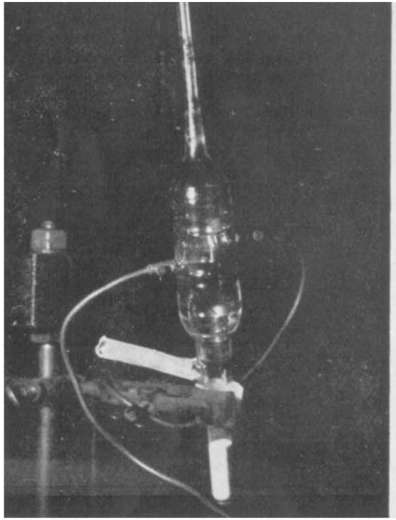
In the subsequent firing trials already eight of the bulbs have been proved, the other two being kept untried in reserve. In each of the eight bulbs so far tried, a condenser of variable capacity charged at 1000 volts was discharged through the medium, which, while always withstanding a discharge of anything up to 0·5 microfarad capacity (total discharge energy = 0·25 Joule), was invariably exploded by one of 1 microfarad capacity, the minimum capacity required for ignition being *circa* 0·75 microfarad. In each case flame filled the vessel more rapidly than the eye could follow, the resulting percentage combustion varying between about 74 and 89 in different experiments.

On 11th November 1927 Dixon witnessed the explosion of one of these bulbs (No. 5) for which the drying period had been 555 days, and which on the previous day had withstood a discharge of 0·5 microfarad at 1000 volts without any sign of ignition. It was eventually exploded by a charge of double that capacity at the same voltage, the resulting combustion being 87·8% complete—a most convincing result, as Dixon freely acknowledged.

The visible features of these highly significant experiments may best be conveyed to readers by the three photographs (Plate I) obtained in the case of bulb No. 6, for which the drying period had been 758 days. No. 1 shows the bulb in position for the firing trials, the white phosphoric anhydride in its lower part being plainly visible; No. 2, taken in a darkened room, shows the non-effect of a discharge passed through the medium from a condenser of 0·5 microfarad capacity charged up to 1000 volts (the spark is the white dot in the centre, and it should be particularly observed that there is not even the faintest indication of any " halo " of combustion round it); No. 3 shows the resulting explosion flame when ignition had been finally effected by a discharge of 1 microfarad at 1000 volts (it should be noted how completely the flame filled the vessel), the resulting combustion being 89·25% complete.

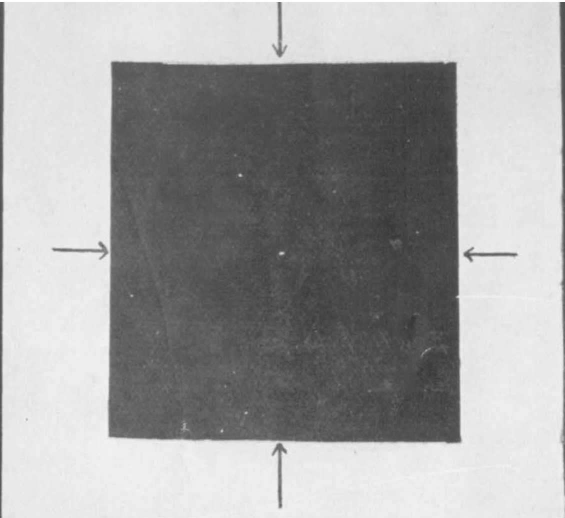
As the ninth such bulb (as yet untried) is before you on the table, we can give you the opportunity of witnessing here and now its behaviour. It was filled on 15th July 1929 with a well-dried $2CO + O_2$ mixture, and therefore its subsequent " drying period " over phosphoric anhydride has extended over 514 days. Its electrodes are now connected with a condenser of 0·25 microfarad charged up to 650 volts. When now it is discharged across the medium in the bulb, you observe that, although the spark is visible to all, no explosion results, because the spark-energy is well below the minimum required for ignition. On increasing the condenser capacity up to 4 microfarads, and again charging it up to 650 volts as before, we shall have stored up about twice the minimum energy required; and on again discharging it through the medium, as you see, an explosion instantly results, the flame rapidly filling the vessel. (On opening the bulb a few days later, it was found that the products contained CO_2, 66·4; CO, 22·0; O_2, 11·1; and N_2, 0·5%, the percentage combustion having been 76 only.) The tenth

PLATE I.



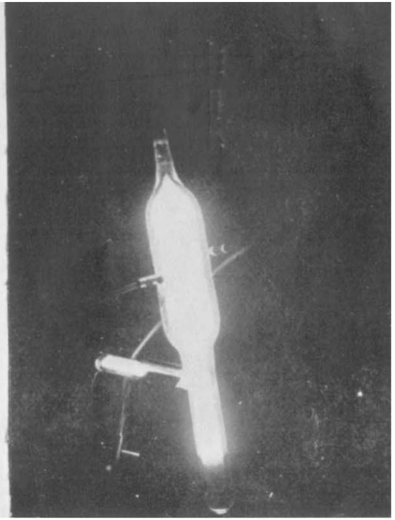
No. 1.

Showing explosion bulb in position for the firing trials.



No. 2.

Showing the non-effect of condenser discharge spark 0·5 m.f. at 1000 volts in bulb. (The spark is the white dot seen at the intersection of the arrows.)



No. 3.

Showing the explosion flame in bulb when ignition had been effected with a condenser discharge-spark of 1·0 m.f. at 1000 volts.

[*To face p.* 354.

PLATE II.

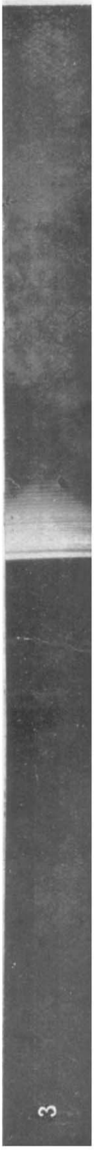
Carbonic Oxide.

No. 1

Hydrogen.

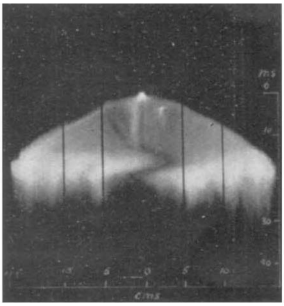
No. 2

CO 53%.
H_2 47%.

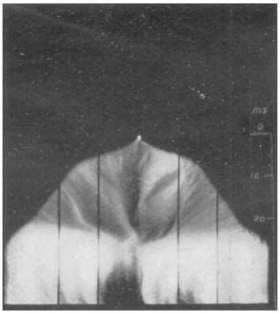


No. 3

PLATE III.

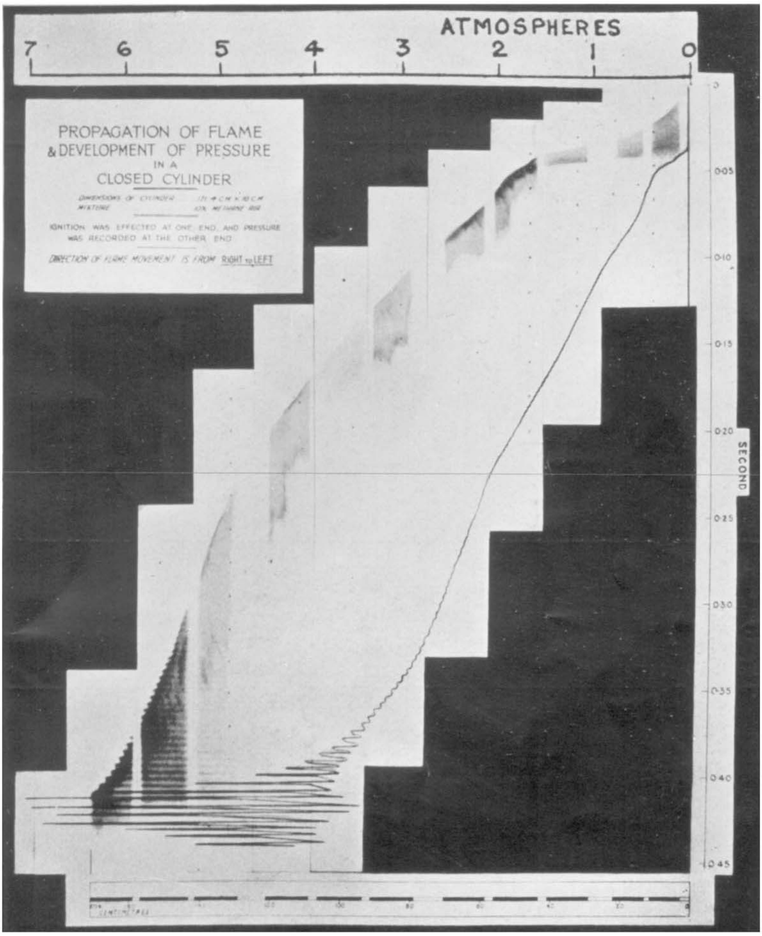


No. 1.



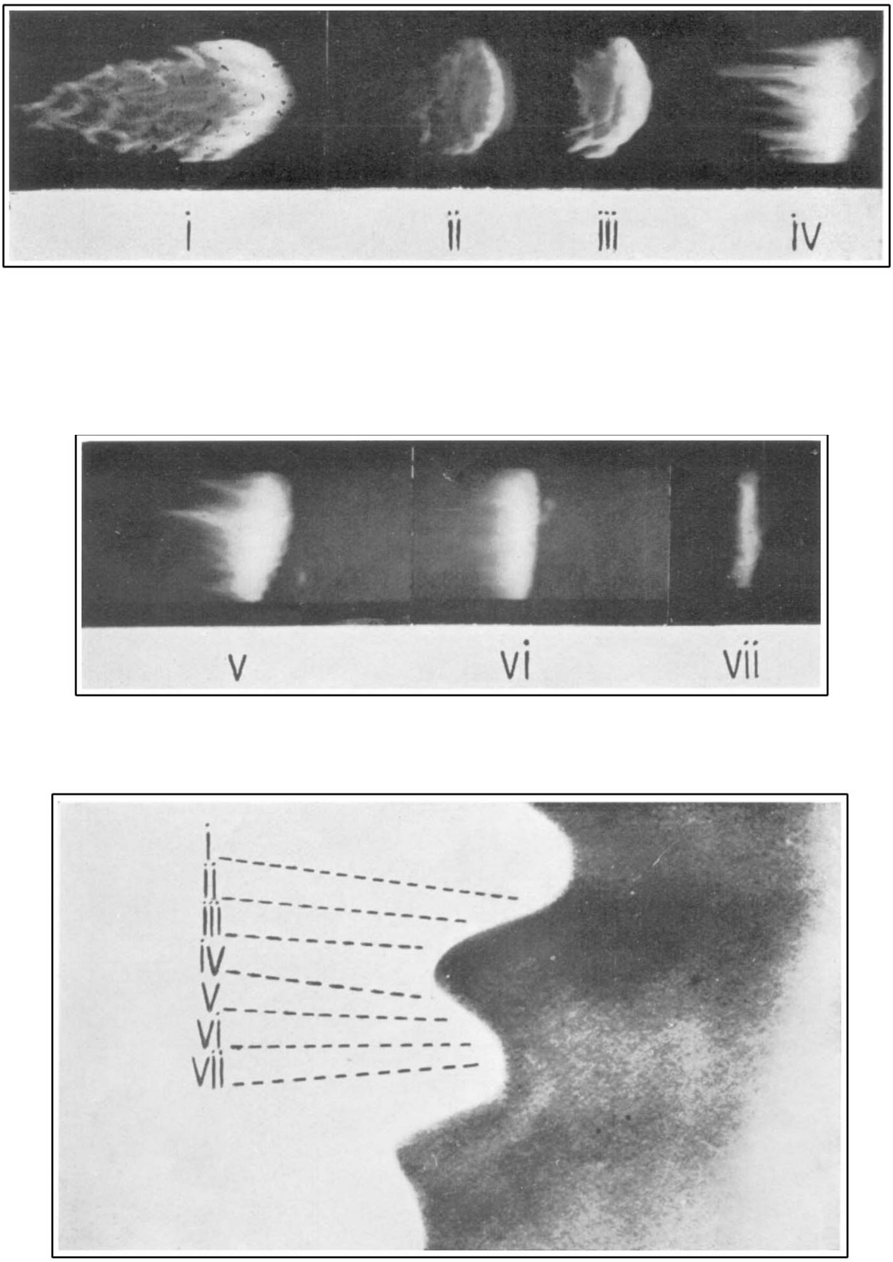
No. 2.

Plate II.



A vibratory explosion of methane and air.

PLATE III.



Analysis of a vibrating flame.

bulb still remains, as yet untried, in reservation for some future occasion.

The conclusion which these experiments enforce is that a highly purified $2CO + O_2$ mixture, dried to the utmost limit possible by means of phosphoric anhydride, can still be inflamed provided that a powerful enough igniting discharge be employed.

(2) *Spectrographic Evidence.*—The fact that the colour and general appearance of a carbonic oxide flame is so different from that of hydrogen, as can be seen from the two exhibited here side by side on the table, has always seemed to me difficult to reconcile with Dixon's original view of the oxidation of carbonic oxide being *wholly* " caused by the alternate reduction and oxidation of water molecules," although it cannot be denied that in presence of steam *some* of it is so burnt.

To elucidate the matter, Dr. Weston (*Proc. Roy. Soc.*, 1925, *A*, **109**, 177, 523) carried out a systematic investigation of the flame spectra of hydrogen and carbonic oxide, as well as of mixtures of the two in different proportions. We were fortunate in having the collaboration of Prof. A. Fowler, one of the foremost living spectroscopists, and three typical spectrograms shown in Plate II (extending from 500 Å.U. in the visible to 2200 Å.U. in the ultra-violet) of flames maintained in an oxygen-rich atmosphere will suffice to show the general character of the results.

No. 1, which is of a flame of pure (undried) carbonic oxide, shows a very strong and apparently continuous spectrum extending over the whole range, with groups of so-called " steam lines " faintly imposed upon it mainly in the region 3200—3060 Å.U. A moderate drying of the gases, or an increase in the pressure up to about ten atmospheres, suffices to suppress these " steam lines " altogether, leaving the continuous spectrum unaffected. Under reduced pressure, the latter is seen to overlie an equally characterised carbon monoxide-banded spectrum, which (as Prof. Fowler said) " is quite distinct from the more familiar oxy-carbon bands which have been observed in vacuum tubes."

No. 2, which is of a flame of pure hydrogen, shows practically nothing except several characteristic groups of " steam lines " in the near ultra-violet, the most prominent being in the 3200—3060 Å.U. region.

The vast difference between these two spectrograms is highly significant. When, however, hydrogen is gradually added to burning carbonic oxide the characteristic continuous flame spectrum of the latter rapidly disappears, and the " steam lines " become more prominent, until when a $50\%CO/50\%H_2$ (" water gas ") composition is reached, the last-named only are visible, as shown in

No. 3. Also, when instead of burning the two gases separately, as is now being done on the table, the two streams are blended and burnt at one orifice as a 50/50 mixture, it will be seen that the flame is hardly distinguishable by the eye from the one in which hydrogen alone is being burnt.

In view of such evidence, it is difficult to resist the conclusion that when undried carbonic oxide burns in undried air or oxygen at ordinary pressure, two sets of reactions occur simultaneously, namely, (*a*) direct interactions between " excited " carbonic oxide and oxygen giving rise to the radiations shown in the continuous and banded parts of the flame spectra, and to the characteristic blue-green colour of the flame, and (*b*) interactions between carbon monoxide and water molecules originating the " steam lines " in the spectrum. On hydrogen being gradually added to the burning gas, the relative proportion of (*a*) to (*b*), which at first is high, rapidly diminishes, until with a 50/50 mixture, (*b*) predominates to the practical exclusion of (*a*). Dixon was greatly impressed by these spectrograms which (he said) constituted " the first clear evidence that in an ordinary carbon monoxide flame both direct and indirect actions are going on at once."

That " excited," though not necessarily " ionised," carbon monoxide is required for (*a*) is indicated by much cumulative evidence, notably that derived from the study of carbonic oxide–air explosions at high initial pressures, as well as from recent determinations (*Proc. Roy. Soc.*, 1931, *A*, **130**, 542) of flame speeds over the whole explosion range of moist carbon monoxide–oxygen mixtures which show, both in the initial slow " uniform " period and in detonation, a marked maximum at about the $3{\cdot}8CO + O_2$ composition, which point is but little altered by dilution with nitrogen, argon, or helium.

In this connexion it should be mentioned that there is now a considerable body of evidence that hydrogen is more effective than its equivalent of steam in promoting the combustion of carbonic oxide; also that their influence is at least two-fold, *i.e.*, physical in very small and chemical in fairly large concentrations, and, as regards the latter, it seems probable that more than one mechanism may be at work. Moreover, the direct oxidation of carbonic oxide is so greatly favoured by pressure that at fairly high pressures it occurs almost exclusively, though even so it may be physically promoted by minute proportions of steam. From private correspondence, as well as from a published letter of his (*Nature*, 1928, **122**, 805), I believe that Dixon was substantially in agreement with such view.

(3) *Combustion in Electric Discharges.*—Reference must also be

made to the independent work of my colleague Professor G. I. Finch and his collaborators upon the " cathodic combustion " of carbonic oxide (*Proc. Roy. Soc.*, 1929, **124**, 303; **125**, 352; 1930, **129**, 314, 656), because it has thrown much-needed light upon the possible ways in which the gas might be burnt in ordinary flames. While agreeing with us that unexcited carbonic oxide and oxygen molecules are mutually inert, they conclude that for the direct oxidation both " excited " (but not " ionised ") carbonic oxide and atomic oxygen are required. Also they suppose an " auto-oxidation " of carbonic oxide—$2CO = C + CO_2$—as possible, the carbon then combining with oxygen, forming monoxide directly. As regards the rôles of steam and hydrogen, they consider that the latter burns to peroxide and " excited " steam, both of which can oxidise carbonic oxide more readily than does oxygen, although " unexcited " steam is relatively inert. All these, and perhaps other, possibilities will have to be considered in future discussions, the issues being more complicated than were formerly supposed. Perhaps a solution may be found in supposing that increasing degrees of " excitation " of the carbon monoxide molecule are needed for its oxidation by hydrogen peroxide, steam, and oxygen, respectively, in somewhat the order named, and that possibly some " excitation " of one or more of these may also be required.

(4) *Photographic Evidence.*—The analysis of explosion flames by the photographic method originated by Mallard and Le Chatelier fifty years ago—afterwards further developed and improved by H. B. Dixon and his collaborators in the " nineties," and recently brought to a still greater precision by Mr. R. P. Fraser, with his new high-speed cameras, in our laboratories—is now so powerful a research weapon that its revelations concerning the effects of progressive drying upon flame propagation through $2CO + O_2$ mixtures will fittingly conclude this review.

It may be recalled that in principle the method consists in photographing the flame moving with velocity x along a horizontal glass tube upon a sensitive film moving in a vertical plane with known velocity y, the graph representing the resultant of the two velocities.

(a) *The influence of progressive drying upon flame speeds, etc.* Of the numerous beautiful photographs taken by Mr. Fraser (*Phil. Trans.*, 1929, *A*, **228**, 202), there are four reproduced in Plate III of particular interest, in which the movements of an explosion flame through a $2CO + O_2$ medium at atmospheric pressure along a horizontal tube (Fig. 6) (35 cm. long × 2 cm. internal diameter) were analysed on a film moving vertically at a constant velocity of 148 cm. per second in the first three, and at 94 cm. per sec. in the fourth. In each case ignition was by means of a condenser discharge across

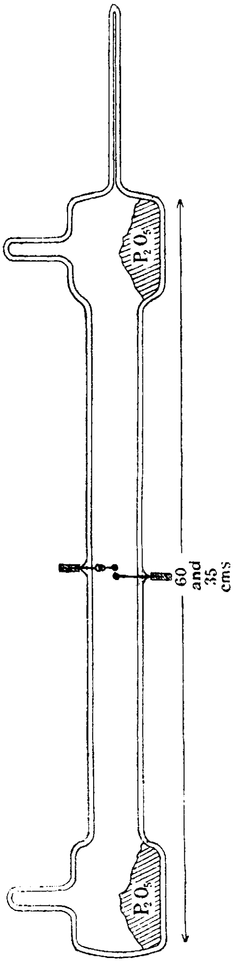


FIG. 6.

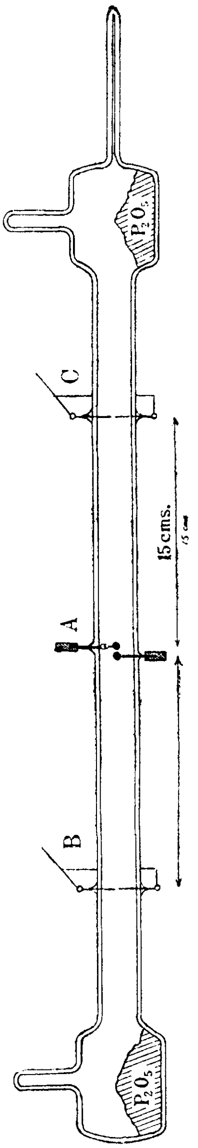


FIG. 7.

platinum poles fixed mid-way along the tube, from which point two explosion flames traversed the mixture in opposite directions towards each end.

In No. 1—*with a* "*moist*" $2CO + O_2$ *medium* ($H_2O = 1{\cdot}7\%$)—the two flames started off immediately from the igniting spark, their initial movements being accelerated up to " shoulders " about 5 cm. along the tube, but afterwards proceeded much more slowly, with almost uniform speeds of about 1200 cm. per sec. towards each end of the tube, the flame fronts being serrated all the way and combustion 100% complete.

In No. 2—with a 7-days $CaCl_2$*-dried* $2CO + O_2$ *medium* (H_2O = 0·03%)—there was, as compared with No. 1, a marked retardation of combustion, the almost uniform flame speeds after the first " shoulder " being reduced to 420 cm. per sec. with combustion only 97·2% complete, and a total duration of luminosity almost double that in No. 1.

No. 3—*with an* 80-*days* P_2O_5*-dried* $2CO + O_2$ *medium*—shows how enormously combustion was further retarded by the removal of the last 0·03% of moisture from the medium, for the total duration of luminosity was now about 14 times longer than in No. 1, and nearly 8 times longer than in No. 2, and the percentage combustion 89 only.

In No. 4—*with a* 223-*days* P_2O_5*-dried* $2CO + O_2$ *medium*—the extreme limit of phosphoric anhydride-drying had been reached, with further slight retardation of combustion; notwithstanding this, the flames ultimately reached the ends of the tube, the percentage combustion being 92, and the total duration of combustion about 15 times longer than in No. 1, and more than 8 times longer than in No. 2.

The following data have been deduced from the photographs :

	No. 1.	No. 2.	No. 3.	No. 4.
Time (in millisecs.) for flames to reach ends of tube	16·9	23·6	287	308
Total duration of luminosity (millisecs.)	27·5	50·0	388	416
Percentage combustion	100	97·2	89	92

(b) *The influence of a strong electric field upon flame propagation through an intensively-dried* $2CO + O_2$ *medium.* (i) On repeating the experiment (No. 4) with a 245-days phosphoric anhydride-dried $2CO + O_2$ medium, but in a longer (60 cm.) tube, the slow initial flame movements could be followed by the eye, until (as shown in Plate IV, No. 5) they were arrested and remained almost stationary for about 53 millisecs. Then followed further very slow advances in each case up to a point about mid-way between that of ignition and the end of the tube, after which the flames retreated slightly into the partly burnt medium behind them, where they were extinguished. The mean flame speeds were only 72 cm. per sec., and although combustion lasted 554 millisecs. in each case, only 26·5% of the total mixture in the tube was burnt.

(ii) It next occurred to us that, supposing the first accelerating influence of moisture upon the direct oxidation of carbonic oxide to be electrical rather than chemical, a repetition of No. 5 experiment with the super-imposition of a strong electric field upon the intensively-dried $2CO + O_2$ medium at and after the moment of ignition should reveal some difference in the behaviour and propagation of the resulting flames. Accordingly, an exactly similar explosion tube filled with the dry $2CO + O_2$ medium was prepared, but with two supplementary wires sealed in 30 cm. apart with the central firing point exactly mid-way between them, as shown in Fig. 7. After allowing a 240-days " drying-period " over the phosphoric anhydride situated at each enlarged end of the tube, the medium was fired centrally, precisely as before, the pair of supplementary wires being connected with the two poles, respectively, of a Wimshurst machine which was operated throughout the ignition and subsequent burning. From photograph No. 6 (Plate IV) it will be seen that the two flames started off in opposite directions from the igniting-spark with, during the first 100 millisecs. or so, extremely slow and almost uniform velocities of 43·5 and 50 cm. per sec., respectively; this initial phase was then succeeded by another of such marked progressive accelerations in the two oppositely-moving flame fronts as they approached and traversed the electrodic regions of the field that they quickly reached the end of the tube; whereupon their luminosities increased and extended backwards until nearly the whole tube was filled with flame. The total duration of luminosity, from beginning to end, was 375 millisecs., and the percentage combustion was 89·6. Another significant feature was that initially the flame travelled more quickly towards the *negative* than towards the *positive* pole of the field.

Commenting upon these last two photographs, Dixon, who had followed the experiments with the closest interest, said that " it was evident that the resistance to combination offered by the dryness of the gases could be overcome by the electrostatic field, and apparently this relief was more easily given by one pole than the other . . . (so) that the problem presented by the burning of this gas has become one of the most interesting in physical chemistry " (*Nature*, 1929, **124**, 582). And with these, his last published words upon it, my story is ended.

Yet one word more is due to his memory. Dixon was not only himself a great exponent of the experimental method, but also a master-trainer of those who were privileged to be his pupils in research; and his chief fame will be that he established in this country a school of combustion research embodying the traditions of Robert Boyle and Humphry Davy, with whom he ranks in an apostolic succession. In a letter which he wrote me on 26th August, 1927, about the publication of " Flame and Combustion in Gases," which had been dedicated to him, he said : " I think you know that

I regard the chief reward of my work to lie in the fact that, when I started fifty years ago to repeat Bunsen's experiments, no one in England seemed to care about the burning of gases, and now there is an active English school, largely made up of old students . . . really keen on the fundamental study of gas reactions."—VALE MAGISTER PRAECLARE !