

XLVI.—*The Mode of Formation of Carbonic acid in the burning of Carbon Compounds.*

By Professor HAROLD BAILY DIXON, M.A., F.R.S.

THE usual statements concerning the burning of carbon compounds, namely, that the carbon unites directly with oxygen to form carbonic acid, and that this is reduced in presence of an excess of the carbon to carbonic oxide, appear to have little or no experimental foundation. All the direct evidence points the other way.

But with regard to the mode in which carbonic acid is formed, and the part played by moisture in its formation, the evidence is curiously puzzling. Granting that carbon in any compound may burn with oxygen to carbonic oxide, we have to deal with the following facts:—

1. An explosion is not propagated by a spark in a dried mixture of carbonic oxide and oxygen at ordinary temperature and pressure (Dixon, *Brit. Assoc. Report*, 1880, 503).

2. When a long tube full of the dried gases has moisture introduced at one end and the gases are ignited there, the flame traverses

the moist gases, but dies out on reaching the dry gases (Dixon, *Chem. News*, 1882, **46**, 151). The flame of dry carbonic oxide burning in air is extinguished by plunging it into dry air (M. Traube, *Ber.*, 1885, *b*, 1890).

3. The addition of steam increases the rapidity of inflammation of carbonic oxide and oxygen, both in the ordinary flame and in the explosion-wave (Dixon, *Phil. Trans.*, 1884, Pt. 2, 640, and 1893, A, 111).

4. Carbonic oxide and oxygen appear to be inert towards one another in the incomplete combustion of hydrogen and carbonic oxide; at all events, they act as if they were incapable of rapidly uniting (Dixon, *Phil. Trans.*, 1884, Pt. 2, 671).

5. Dried carbon does not glow when heated in dried oxygen; it burns, however, to carbonic oxide. In the presence of finely divided platinum, carbonic acid is formed (Baker, *Phil. Trans.*, 1888, A, 571).

6. Dried carbonic oxide and oxygen will unite in the path of the electric spark (Lothar Meyer, *Ber.*, 1886, **19**, 1099; Beketoff, *Bull. Acad. St. Pétersbourg*, [N.S.], **2**, 175; Dixon). The amount of combination depends upon the nature of the spark; a limit is reached when the rate of combination is equal to the rate of decomposition of the carbonic acid formed (Dixon and Lowe, *Trans.*, 1885, 571).

7. The dried gases completely combine, without producing flame, in contact with a heated platinum wire (Dixon and Lowe, *Trans.*, 1885, 576).

8. Dry carbonic oxide proceeding from a half-burnt cyanogen flame will burn in dried air, provided the two flames are close together (Smithells and Dent, *Trans.*, 1894, 603).

9. An explosion of cyanogen and oxygen will cause the union of dry carbonic oxide and oxygen with which they are mixed (Beketoff, *Bull. Acad. St. Pétersbourg*, [N.S.], **2**, 175).

10. In the explosion of cyanogen with an excess of oxygen, the formation of carbonic acid is complete, and is not affected by the presence of moisture (Dixon, *Trans.*, 1886, 384). The complete combustion of cyanogen, however, does not take place so rapidly or with such violence as the incomplete combustion to carbonic oxide (Dixon, Strange, and Graham, *Trans.*, 1896).

11. Moisture is active in the oxidation of other substances, *e.g.*, sulphur and phosphorus (Baker, *Phil. Trans.*, 1888, A, 581); it also affects the combination of other substances (Cowper,\* *Trans.*, 1883, 153; Baker, *Trans.*, 1894, 611; Pringsheim, *Ann. Phys. u. Chem.*,

\* The effect of moisture in determining the combination of chlorine and sodium, the discovery of which is usually attributed to Wanklyn, is not mentioned by Wanklyn in his paper (*Chem. News*, **20**, 271).

[N.F.], **32**, 384), and facilitates the passage of the electric discharge in gases (J. J. Thomson, *Phil. Mag.*, [5], **36**, 313; *Brit. Assoc. Report*, 1894, 482).

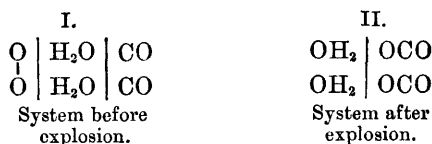
Several explanations have been put forward to account for the influence of moisture in promoting the combination of carbonic oxide and oxygen; some of these have special reference to this reaction only, whilst others are of more general application. Most of the hypotheses advanced have, on examination, suggested experiments by which their probability might be tested. It will, I think, be useful to examine these hypotheses in the light of the evidence which has been accumulated. Even if it should appear, as I think, that no satisfactory explanation has been arrived at, a discussion of the results may focus attention on the essential points of the problem, and may serve to suggest future experiments.

In my papers on the subject I have made no attempt to suggest a reason why oxygen should not explode with carbonic oxide. I have limited myself to the conclusions which seemed to accord most closely with the observations: (a) that carbon burns primarily to carbonic oxide; (b) that carbonic oxide is inert, under ordinary conditions, towards oxygen; and (c) that carbonic oxide at a high temperature decomposes steam to form carbonic acid and hydrogen, so that, in the ordinary explosion of moist carbonic oxide and oxygen, the steam acts catalytically as a carrier of oxygen.

It is evident, from the results recorded in the previous paper on "The Explosion of Cyanogen," that the second conclusion (b) must be modified. Under certain conditions, carbonic oxide and oxygen unite readily. We are confronted, therefore, with the apparent anomaly—two gases which are not exploded by the spark or application of a flame, which are inert, or do not unite rapidly, as other gases do, in explosions, nevertheless combine in presence of heated platinum, and in presence of other combining gases, or if one of them has just been formed by a chemical reaction.

Professor H. E. Armstrong,\* taking a wide survey of the conditions of chemical combination, considers the function of the steam in the explosion of carbonic oxide and oxygen to be that of the liquid in a galvanic cell. The two gases, inert in the pure state, require "the formation of a conducting system in which electrolysis can occur." Comparing the system of carbonic oxide, steam, and oxygen to a Grove gas battery, Armstrong regards the oxidation of the carbonic oxide by the oxygen of the water as dependent upon the simultaneous oxidation of the hydrogen of the water by the free oxygen.

\* "Presidential Address to Chemical Section, British Association, 1885," *Proc. Roy. Soc.*, 1886, **40**, 287; *Trans.*, 1886, **49**, 112. "Presidential Address to Chemical Society," *Trans.*, 1895.



The general theory advocated by Armstrong is that interaction does not occur between two pure substances, and that water will condition the interaction between them only if it be capable of forming a composite electrolyte with one of them. I am not sure whether Armstrong considers that water forms a composite electrolyte with carbonic oxide, or whether water itself is the electrolyte; but, in either case, it is not easy to explain all the facts. The theory, as I understand it, supposes that the three substances, carbonic oxide, steam, and oxygen must be in contact while the change proceeds, and any two of these gases will be inert on meeting. If, therefore, we accept the molecular theory of gases, the change will only occur on the simultaneous collision of molecules of the three substances; or, taking Armstrong's equation, on the simultaneous collision of five particular molecules, two of carbonic oxide, two of steam, and one of oxygen. What the chances are in favour of such collisions occurring might, I suppose, be calculated; it is obvious that their number must be exceedingly small, compared with the collisions between any two molecules. Supposing this quintuple collision occurred, the heat evolved by the chemical change would be divided among the products of interaction; the heated steam and carbonic acid molecules so formed would fly in all directions, and inevitably some steam molecules would come into violent collision with unburnt carbonic oxide molecules. What would happen? Experiment shows that if we heat carbonic oxide and steam together, they react, forming carbonic acid and hydrogen. Do they do so in the case supposed above? If they do, carbonic acid is formed in a manner independent of electrolytic conduction. If they do not, how are we to explain the action of heat on carbonic oxide and steam?

Again, the electrolyte theory has to explain the oxidation of carbonic oxide in the burning of cyanogen. As we have seen, moisture does not appear to be necessary for this reaction or to appreciably affect the result if present. I have tried an experiment to see whether some oxide of nitrogen, which might be formed in the initial combustion of the cyanogen, can act the part of "catalyst" between carbonic oxide and oxygen. Peroxide of nitrogen I found to have no effect; nitrous oxide I had previously tried with the same result.

But apart from these difficulties, we must bear in mind that an explosion in moist carbonic oxide and oxygen is propagated at a

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velocity of over 1700 metres per second. This velocity of explosion, though inferior to that of hydrogen and oxygen, is comparable with that of hydrogen and chlorine, an explosive mixture in which the flame is propagated though the gases be carefully dried. The rate of the explosive wave in gases approximates, according to M. Berthelot's theory, to the mean rate of movement of the products of combustion before they have lost any heat, or, according to my hypothesis, to the velocity of sound in the burning gases, which is equal to the mean rate of the *forward* movement of the reacting molecules.

Without insisting on the exactness of these theories, we may ask whether it is more probable that the flame is propagated at such velocities from molecule to molecule, or whether the flame can only advance as simultaneous collisions occur of five particular molecules out of three sets? In our present state of knowledge, I believe the former view presents far fewer difficulties, and accordingly I think we are not yet warranted in applying the electrolytic theory to explain the reactions of gases *at high temperatures*.

Professor J. J. Thomson, who has made experiments of remarkable interest on the electrolysis of gases, has given us a theory as to the function of water in the explosion of carbonic oxide and oxygen. Finding that the presence of a trace of aqueous vapour in a gas greatly facilitates the passage of the electric discharge, and permits a phosphorescent glow to be formed in the gas after the discharge has passed, Thomson compares these phenomena with the effects of moisture on chemical combination. If the first discharge through a gas is accompanied by a splitting up of some of the molecules we can see, he says, "why a cause which increases the facility with which the first discharge passes through the gas should also increase the tendency of the gas to enter into chemical combination." The theory, as I understand it, is this: Pure water, though not a conductor, has such a high specific inductive capacity that its electrostatic effect is much the same as if it were a conductor. A molecule of two oppositely charged atoms, coming close to the sphere of liquid water, might be dissociated owing to the power which the atoms would possess of unopposed movement along the surface of the sphere. Such separated atoms would be more ready to enter into chemical combination than the undecomposed molecule.

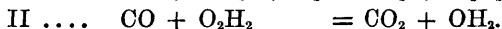
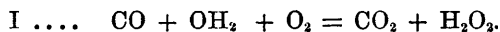
In order that this dissociation of molecules should be brought about, the presence of drops of liquid water is necessary. They might be condensed only for an instant and then evaporate. This formation of transitory drops of water is to be expected, Thomson says, even when the vapour is far below saturation. But to explain the combination of carbonic oxide and oxygen in the explosion-wave, a trace of steam far below saturation at ordinary temperatures would

have to be condensed into liquid particles at a temperature which has, I believe, never been estimated below  $3000^{\circ}\text{C.}$ , and is probably very much higher. But perhaps I have misunderstood Thomson's meaning. Should it be supposed that the vapour really does its work of dissociation in the unburnt gas, leaving, by alternate condensation and evaporation, loosely combined atoms of oxygen which combine with carbonic oxide when the explosion reaches them? According to this view, the work of the moisture would be preparatory. But it must be remembered that a small quantity of hydrogen, or other inflammable gas, containing hydrogen, confers inflammability on the mixture. Now, this hydrogen only forms steam when the explosion reaches it; nevertheless, it enables the carbonic oxide to burn. In this case, the steam molecules must exert their influence in the flame itself, and not in the cool unburnt gas.

Thomson states that oxygen when carefully dried shows no phosphorescence after the discharge; air, on the other hand, is made phosphorescent by carefully drying. If this power of phosphorescing is connected with the dissociation of the atoms, as is suggested, we should expect carbonic oxide to burn in dry air. But experiment shows that the carbonic oxide flame is more readily extinguished in dry air than in dry oxygen.

But while I hold that the effect of moisture in transmitting an explosion in carbonic oxide and oxygen has not been shown to be due to an electrolytic or to a dissociating action on the part of the water, I believe these influences may be at work in the interaction of gases at ordinary temperatures,\* such as have been studied more particularly by Brereton Baker. The influence of platinum in determining the union of dry carbonic oxide and oxygen may be due to the conductivity of the metal, or, on the other hand, to its attraction for oxygen. There is perhaps a danger lest in seeking for general laws we may miss some simpler explanation.

Moritz Traube (*Ber.*, 1885, *b*, 1890) in 1885 advanced the hypothesis that the function of the steam in the explosion is to yield its atom of oxygen to the carbonic oxide at the same time that its hydrogen unites with a molecule of oxygen to form hydrogen peroxide, and that the latter interacts with more carbonic oxide to reform steam and carbonic acid:—



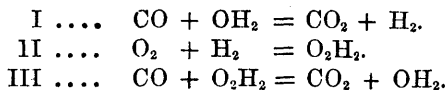
I have dealt fully with this hypothesis in a former communication

\* I have shown that oxygen does not combine with sulphurous oxide in presence of steam at temperatures up to  $100^{\circ}\text{C.}$ ; in presence of particles of liquid water, oxidation takes place, *Journ. Gas Lighting*, 1881, **37**, 704.

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to this Society (Trans., 1886, **49**, 94), Since it was put forward mainly on the mistaken ground that carbonic oxide was not oxidised by steam at a high temperature, the refutation of this error removed the chief argument in its favour.

Mendeléeff (*Principles of Chemistry* (Eng. Ed.), 1891), rejecting Traube's first equation, considers that the carbonic oxide is oxidised directly by the steam, but thinks that the liberated hydrogen combines with a molecule of oxygen to form hydrogen peroxide, which in turn is reduced by more carbonic oxide.



This opinion is grounded on his conviction that gases enter into combination in equal volumes, and that the apparent exceptions to this law of nature are to be accounted for by supposing that such reactions are in reality complex, the initial reactions being between equal volumes. The law that *reactions of equal volumes precede all others* affords the simplest explanation, according to Mendeléeff, of the necessity for the presence of steam to bring about the union of carbonic oxide and oxygen, since the direct oxidation of carbonic oxide by oxygen would involve an action between unequal volumes of gases.

As an instance of the application of this law, we may glance at Mendeléeff's suggestion that the synthesis of ammonia takes place through the initial formation of  $\text{N}_2\text{H}_2$ , which, in turn, unites with its own volume of hydrogen to form hydrazine,  $\text{N}_2\text{H}_4$ , which finally breaks up into nitrogen and ammonia. Without discussing the general validity of the law which Mendeléeff here lays stress upon, it will be sufficient for my immediate purpose to refer to an experiment which I have made with carbonic oxide and nitrous oxide. These gases, mixed in equal volumes over mercury in the ordinary way, are readily exploded by a spark. According to Mendeléeff's view, there is nothing to prevent these gases, when dry, from interacting, since equal volumes are concerned. Actually, they resist the action of the spark when well dried; the addition of a trace of water renders them readily explosive again. The influence of steam does not appear, therefore, to be explained by the law of equal volumes.

The late Professor Lothar Meyer (*Ber.*, 1886, **19**, 1099), who was one of the first to repeat the experiment with the dried gases, put forward the view that it was the high temperature required for the ignition of carbonic oxide and oxygen—compared with the temperature at which carbonic oxide reacts with steam—that favoured the



combination of the moist gases. If a very high temperature were required for the ignition of carbonic oxide and oxygen, and a lower temperature for the action between carbonic oxide and steam, the latter would occur with greater readiness in the neighbourhood of the spark; and if the liberated hydrogen could combine with oxygen at a low temperature also, steam would be reformed and the process would be repeated by the alternate reduction and oxidation of steam. Adopting my view as to the course of the chemical changes occurring, Lothar Meyer explains them on the ground that the direct oxidation requires a far higher temperature than the indirect action; he found that a very powerful spark, driven lengthways through a column of dried carbonic oxide and oxygen, would bring about the union of the gases, and that in a stream of strong sparks complete combination took place in a short time. He attributes the combination to the very high temperature of the spark, which is not maintained except in the path of the discharge, and so the incipient explosion set up in the path dies out around it. In favour of this view, he quotes my own observations on the limits of dissociation of carbonic acid by the electric spark, and the combination of dried carbonic oxide and oxygen by heated platinum (*Trans.*, 1885, 571). With a feeble discharge, the dissociation of carbonic acid is greater than when the sparks are strong. Again, when a platinum wire is heated in a mixture of dried carbonic oxide and oxygen, the wire glows intensely, and complete combination takes place without flame on the surface of the platinum. The platinum, according to Lothar Meyer, supplies the heat necessary for direct combination.

Mallard and Le Chatelier (*Mélanges Gazeux explosifs*, 7, found the ignition point of hydrogen and oxygen to be about  $550^{\circ}$ , and that of carbonic oxide and oxygen to be about  $650^{\circ}$ . Victor Meyer and Freyer (*Zeit. physikal. Chem.*, **11**, 28) found that the ignition point of hydrogen and oxygen, in a closed bulb, lay between  $530^{\circ}$  and  $606^{\circ}$ , whilst that of carbonic oxide and oxygen lay between  $650^{\circ}$  and  $730^{\circ}$ . On the other hand, Naumann and Pistor (*Ber.*, **18**, 2894) found that carbonic oxide was not oxidised by steam below  $600^{\circ}$ , but oxidation began between  $602^{\circ}$  and  $634^{\circ}$ . These observations so far agree with Lothar Meyer's explanation that they show that carbonic oxide and oxygen do not explode until a temperature is reached at which the carbonic oxide could be oxidised by the steam present, and the liberated hydrogen could reform steam. But I think no satisfactory evidence has been adduced to show that it is merely owing to an insufficient temperature being reached that an explosion is not propagated in dry carbonic oxide and oxygen. At first sight, the results obtained in the explosion of cyanogen seem to favour Lothar Meyer's view; for the carbonic



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oxide produced in the wave-front must be at a very high temperature, and it is found to combine with the oxygen present. Although, it might be argued, the explosion is not propagated in dry carbonic oxide and oxygen at ordinary temperatures, nevertheless, when these gases are mixed together in a very highly heated state, as they are in the combustion of cyanogen, then the two gases can unite explosively. But this is not really the case. If the carbonic oxide only required a high temperature to unite with oxygen, it should do so the moment after it is formed, for it is then at its maximum temperature. The immediate formation of carbonic acid should ensue from the collisions between oxygen molecules and the highly heated carbonic oxide molecules formed in the wave-front. Thus the complete combustion of cyanogen would be rapidly effected, and the temperature reached would be far higher than in the incomplete combustion. Now both the photographs of the flame and the rates of explosion show that this complete combustion does not take place immediately on the explosion of cyanogen; on the contrary, the extra oxygen appears to be inert in the wave-front, and only combines gradually behind the wave.

Again, if Lothar Meyer's view is correct, a considerable increase in temperature of one of the gases might be expected to increase the inflammability of carbonic oxide in air. As Traube first demonstrated, an ignited jet of carbonic oxide, dried by oil of vitriol, is extinguished on being plunged into a jar full of air dried in the same way; the flame is usually put out an inch or two from the mouth of the jar. The same result is found when the stream of carbonic oxide is strongly heated before it burns. The glass tube bringing the gas from the drying towers was luted by means of asbestos and soluble glass to a platinum tube 6 in. long. Round a length of 4 in. of the platinum an asbestos jacket was fitted, and the whole was heated strongly by two blow-pipe flames. At a bright red heat the blue colour of the carbonic oxide flame burning in the air at the mouth of the tube changed to a pinkish-orange. On plunging the flame into the jar full of dried air, it was extinguished quite as readily as it was without heating. On withdrawing the tube from the jar the gas immediately rekindled on meeting the ordinary air. The experiment was repeated several times with hot and cold gas alternately, and always with the same result. The high temperature of the carbonic oxide in no way increased its inflammability in dry air.

Apart, therefore, from the difficulty of understanding how a flame of burning carbonic oxide and oxygen, which has, at least, a mean temperature of  $3000^{\circ}$ , is extinguished in the dried gases, owing to the temperature not being high enough, or how the intensely heated carbonic oxide formed in the explosion of cyanogen does not burn in

the wave-front, whilst a red hot platinum wire is admittedly hot enough to bring about the combination, we have some direct evidence to show that the non-explosibility of carbonic oxide and oxygen is not simply a result of insufficient temperature.

M. Beketoff (*Bull. Acad. St. Pétersbourg*, [N.S.], 2, 175) has sparked a dried mixture of carbonic oxide and oxygen, and found that carbonic acid was gradually formed; he has also brought about the union of the dry gases by mixing 10 per cent. of cyanogen with them and then exploding. M. Beketoff's view of the function of the moisture is that it acts by reason of the ready dissociation of its molecule into hydrogen and an atom of oxygen which combines with the carbonic oxide. Steam begins to dissociate at  $800^{\circ}$ , he says, oxygen is stable at  $2000^{\circ}$ . "The molecules of steam furnish the atomic oxygen which is indispensable for the combustion of carbonic oxide more readily than the molecules of oxygen themselves." But of course this theory only puts off the difficulty one stage. If carbonic oxide has not the power to break up oxygen, why should the liberated hydrogen be able to do so? The heat of formation of carbonic acid from carbonic oxide is greater than the heat of formation of steam from hydrogen. M. Beketoff only leaves us with a greater difficulty to explain.

The experiment, made by M. Beketoff, of firing cyanogen and oxygen mixed with carbonic oxide and oxygen, in the dry state, is of considerable interest, since it shows that the burning of the cyanogen affects the union of the carbonic oxide with which it is in contact. He considers that this result is due to the high temperature produced by the burning cyanogen; this high temperature, he thinks, by breaking up the oxygen molecules causes the carbonic oxide to burn. M. Beketoff does not say that he analysed the residual gases; had he done so, he would probably have found that the combustion was not complete. Some years ago (in 1884), I tried the effect of mixing some carbon bisulphide vapour with carbonic oxide, and with enough oxygen to burn them both. After the gases had been well dried, a spark produced a flame which traversed the whole column of gases, but only caused a partial combustion of the carbonic oxide.

I have lately repeated these experiments, using different quantities of carbon bisulphide and cyanogen. Mixtures of carbon bisulphide with oxygen and with nitrous oxide sufficient for complete combustion were prepared and allowed to stand over mercury in contact with phosphoric oxide; a mixture of cyanogen with twice its volume of oxygen was also dried in the same way. Into tubes, containing some 40 c.c. of a mixture of carbonic oxide with oxygen or with nitrous oxide over mercury, phosphoric oxide was introduced, and the gases were allowed to dry for a week; they were then tested by

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sparks.\* Into several tubes containing the non-inflammable mixture, portions of the explosive mixtures were introduced, and the gases allowed to diffuse for 24 hours; a spark was then passed.

In the first experiment, a dried mixture of carbon bisulphide and nitrous oxide ( $\text{CS}_2 + 6\text{N}_2\text{O}$ ) was added little by little to a dried mixture of carbonic oxide and nitrous oxide ( $\text{CO} + \text{N}_2\text{O}$ ). When 17.6 per cent. of the carbon bisulphide mixture had been added, the gas did not inflame, but when 20 per cent. had been added, the spark produced a flame which traversed the tube. The carbon bisulphide formed 2.8 per cent. of the total mixture. After the absorption of sulphurous oxide by manganese peroxide, and of carbonic acid by potash, the residual gas exploded violently on passing a spark. The analysis showed that the combustion of the carbon bisulphide was not complete,† and over 90 per cent. of the original carbonic oxide had escaped combustion in the first explosion.

In a second experiment, the composition of the mixture was

CO .....	56
$\text{CS}_2$ .....	4
$\text{O}_2$ .....	40

After explosion, it was found that 13.8 per cent. of the original carbonic oxide was unburnt.

In a third experiment, the composition of the mixture was

CO .....	45
$\text{CS}_2$ .....	8
$\text{O}_2$ .....	47

The combustion was practically complete at the first explosion.

Two cyanogen mixtures were made. In the first experiment, the composition of the mixture was

CO .....	53.3
$\text{C}_2\text{N}_2$ .....	6.7
$\text{O}_2$ .....	40.0

\* In two of the tubes so tested, the third or fourth spark set up a flame which traversed the whole column of gas, and appeared to linger some time at the bottom of the column where the phosphoric oxide was lying. The analysis of the gases showed that in one case 37 per cent., and in the other 50 per cent., of the carbonic oxide remained unburnt.

† The escape of some of the readily combustible  $\text{CS}_2$  shows that an inflammable gas, together with an excess of oxygen, may pass through a flame.

Professor Smithells (Trans., 1894, 65, 608) found that some unburnt cyanogen passed through the inner cone of a cyanogen-air flame, although some carbonic acid was also being produced in the flame. I see no difficulty in the view that the cyanogen burns to CO in the inner cone, and this CO begins to be oxidised to  $\text{CO}_2$  before all the cyanogen is burnt. The inner cone of the divided flame is burning at constant pressure; the conditions are wholly different from those of the explosion-wave.

that is, the cyanogen detonating gas formed 20 per cent. of the mixture. The spark produced an explosion in which the cyanogen was completely burnt, together with two-thirds of the carbonic oxide. After the absorption of the carbonic acid, the residual gases were exploded, when it was found that 32·3 per cent. of the original carbonic oxide had escaped combustion in the first explosion.

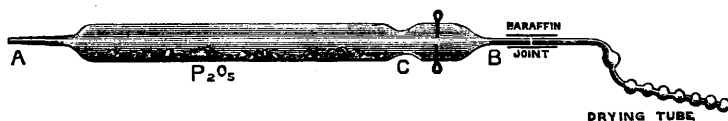
In the second experiment, the composition of the mixture was

CO .....	43·3
C <sub>2</sub> N <sub>2</sub> .....	11·7
O <sub>2</sub> .....	45·0

that is, the cyanogen detonating gas formed 35 per cent. of the mixture. In the first explosion, 13 per cent. of the original carbonic oxide escaped combustion.

The chief results established by these experiments are—(i) that it is possible to submit the dried mixture of carbonic oxide and oxygen to the intimate contact of a flame without causing complete combustion, and (ii) that the quantity of carbonic oxide burnt depends upon the intensity of the exciting flame.

The opinion advanced by Lothar Meyer and by Beketoff that the dried mixture resists explosion owing to the stability of the oxygen molecule, led me to try the effect of the spark on a dried mixture of carbonic oxide with ozonised oxygen. Some difficulty was experienced in obtaining phosphoric oxide of sufficient purity not to act on the ozone.



The arrangement shown in the figure was finally adopted. The tube AB was constricted slightly at C and drawn out at B. Phosphoric oxide was placed along the tube from A to C, and the tube was then drawn out at A to a very fine point. The end B was connected by a paraffin joint to a long drying tube containing boiled sulphuric acid. A slow stream of oxygen was then sent through the apparatus while the tube was heated below redness in a gas furnace from A to C. The heating was maintained for four days in the stream of oxygen, after which a Siemens' induction tube was inserted between B and the drying vessel. Ozonised oxygen was then passed, and the tube allowed to cool. After the stream of ozone had been kept up for six hours, a mixture of carbonic oxide and highly ozonised oxygen, which had been prepared over sulphuric acid, was passed through the tube so as to displace the gases in it. The fine

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openings at A and C were then closed with paraffin, and the tube allowed to stand for a week. The ozone used in the experiment was prepared by slowly passing oxygen backwards and forwards through a Siemens' induction tube five or six times between two glass gas holders over sulphuric acid; the carbonic oxide was then added.

On passing a spark through the mixture between wires which were 7 mm. apart, there was no explosion, but a considerable halo of blue light appeared round the path of the spark. From an analysis of the gases driven from the tube by a stream of carbonic acid the composition of the mixture was found to be

CO .....	36
Ozone. ....	8
Oxygen and air .....	56

The experiment showed that a considerable quantity of ozone did not confer inflammability on the mixture; the resistance to explosion could not in this case be due to the stability of the oxygen, for sufficient ozone was present to burn two-thirds of the carbonic oxide present.

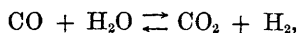
Lastly, I have to discuss a view as to the part played by moisture, which has not the advantage, enjoyed by the electrolytic theories, of embracing many phenomena apparently cognate. This supposes that in the collisions of carbonic oxide and oxygen molecules which occur when the mixture is strongly heated, the more violent collisions do not result in combination because the temperature of the product would be above its dissociation temperature. Steam, however, is not so easily dissociated as carbonic acid. When violent collisions occur between carbonic oxide and steam molecules, chemical change may result, since the heat of formation of carbonic acid from carbonic oxide and steam is small (9,200 cal.). The liberated hydrogen may recombine with oxygen since steam is stable under the conditions. An explosion, in short, is not propagated in the dry gases because the temperature of direct oxidation would be too high; in the presence of moisture, the explosion is propagated owing to indirect oxidation. The theory would *a fortiori* apply to the non-explosion of carbonic oxide and ozonised oxygen, for more heat is given out in the oxidation by ozone than by pure oxygen.

But it might be objected, since the quantity of steam necessary is very small, the amount of heat absorbed by it must be very small, and therefore the temperature reached by the carbonic acid would be practically the same whether it were formed directly in one stage (evolving 68,200 cal.), or in two stages (evolving 9,200 and 59,000 cal.). Although the total heat evolved would be the same in the two cases, the temperature of the interacting molecules might be very

different. In the direct oxidation of carbonic oxide, the heat of formation of 2 mols. of carbonic acid at constant volume would be sufficient to raise their temperature  $8,030^{\circ}$ , while in the indirect oxidation the same heat would be divided between 2 mols. of carbonic acid and 2 mols. of steam. Actually, if the oxidation is effected indirectly by a small quantity of steam, the steam molecules must react over and over again, and must rise in temperature; but the fewer the molecules of steam, the more slowly is the flame propagated, and meanwhile heat is lost by conduction to the walls. Again, it might be urged that dilution with an inert gas, such as nitrogen, should, on this hypothesis, cool the gas sufficiently to allow the formation of carbonic acid. But the molecular heat due to the direct union would for the moment be entirely in the carbonic acid formed, and would only be divided afterwards among the inert molecules.

Although the union of carbonic oxide and oxygen might thus be limited by dissociation, it is not necessary to suppose that in the burning of a damp mixture the oxidation of all the carbonic oxide must be effected by the steam. On the contrary, we can imagine that in the flame the slower collisions between carbonic oxide and oxygen result in the formation of carbonic acid.

With regard to the "inertness" of oxygen towards carbonic oxide in the incomplete combustion of hydrogen and carbonic oxide, I have stated that the phrase must be modified. In the equilibrium set up between the opposite chemical changes,



it was found that the ratio

$$\frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}_2} = \text{a constant},$$

provided that the oxygen taken was not more than enough to combine with the hydrogen in the mixture; with an excess of oxygen the ratio altered. I compared the effect of an excess of oxygen with that of an excess of nitrogen; both altered the ratio in the same sense. Accordingly I explained the alteration by the "inertness" of the oxygen towards the other three gases present, namely, CO, CO<sub>2</sub>, and H<sub>2</sub>O. I now see that the carbonic oxide and oxygen should be capable of combination behind the wave-front, and should not be called inert. But nevertheless the explanation may be in the main correct, for if carbonic oxide and oxygen could only combine together comparatively slowly, the excess of oxygen would retard the completion of the action, and thus have the same effect as an inert gas. According to the dissociation hypothesis, the hydrogen could combine with oxygen in the wave-front, and could reduce carbonic acid, but the carbonic oxide could not combine with the free oxygen until

the gases began to cool down. The period of combination would thus be prolonged just as the cyanogen flame is prolonged by inert nitrogen.

In the explosion of cyanogen with oxygen, the high temperature of the wave-front would prevent the direct union of the carbonic oxide formed there with the free oxygen; behind the wave-front, the carbonic oxide mixed with oxygen would fall in temperature below the dissociation point, and combination would begin. I think this hypothesis explains in a satisfactory way the lower intensity of the cyanogen flame when completely burnt, and the prolonged period during which the gases remain luminous behind the wave-front. I may add that both Bunsen and Deville held that the burning of carbonic oxide was retarded by dissociation.

It has been shown that carbonic acid is formed in the passage of the electric spark through the dried gases. The spark also causes dissociation in dried carbonic acid. It may be supposed in the latter case that the carbonic oxide and oxygen liberated by the heat of the spark partially combine on cooling, while the rest, rapidly mixed with inert gas by diffusion, escapes recombination. When the spark is passed in carbonic oxide and oxygen, the gases in its path, at first too hot to combine, are able to do so as they cool. In a mixture of the three gases, an equilibrium is reached when the rate of combination is equal to the rate of dissociation.

Again, the ready union of carbonic oxide and oxygen without flame on the surface of heated platinum may be explained on this hypothesis if we suppose that the platinum acts as a conductor to carry off the heat.\*

But though the dissociation of carbonic acid explains some of the anomalies that have been discovered, there are still difficulties to be accounted for. In Smithells' experiment of the divided cyanogen flame, it is not easy to see why the carbonic oxide formed in the inner flame should burn in the outer when the flames are near together, but be extinguished on separating the two cones, unless we grant that freshly formed molecules have a power of combination which they lack when they have had time to "settle down." Possibly the heated gases formed by the first flame act like a metallic conductor, but in that case one would expect the flame of burning carbon bisulphide or cyanogen, when mixed with the carbonic oxide, would act in a similar way.

Brereton Baker (Trans., 1894, 617), who has carried out most patient and skilful experiments on the effect of moisture on chemical combination, is of opinion that there is a resistance to the direct union of elements (except in the nascent state), and that moisture

\* An idea suggested by Professor Osborne Reynolds.



facilitates chemical union by allowing the transfer of the opposite electric charges of the molecules. In view of this opinion, and of the experiments lately made by J. J. Thomson, it appeared to me of interest to submit the dry mixture of carbonic oxide and oxygen to the Röntgen rays. Professor Schuster was kind enough to submit my tube to a very active discharge. The gases were contained in a thin soda-lime glass tube fitted with platinum wires. The Röntgen bulb was placed about 10 mm. from the eudiometer. Sparks having been passed through the dried gases without inflaming them, the Röntgen rays were turned on, and from time to time, during a quarter of an hour, a spark was passed through the gases, but no inflammation occurred. To prove the nature of the mixture, a small bubble of hydrogen (less than 0.4 per cent. of the total gas) was admitted to the dried gases. After a few minutes had been allowed for diffusion, a spark was passed, causing a violent explosion. The Röntgen rays, therefore, if they affect these gases at all, are not possessed of marked activity.

While I think the dissociation of carbonic acid at very high temperatures may be regarded as one of the limiting factors in the reaction between carbonic oxide and oxygen, it would seem that there is some other cause limiting the direct combination of these gases at lower temperatures.

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