XI.—*The Combustion of Carbonic Oxide and Hydrogen.*

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PART I.—THE ACTION OF STEAM ON CARBONIC OXIDE.

IN a preliminary account of a research on the incomplete combustion of carbonic oxide and hydrogen, read in 1880 before the British Association, I published the fact that a mixture of carefully dried carbonic oxide and oxygen would not explode when electric sparks were passed through it, but that on the addition of a minute trace of water, or volatile body containing hydrogen, the mixture became inflammable.

To account for this fact, I ventured, after making many experiments, to put forward the hypothesis that, in the ordinary combustion of carbonic oxide, the steam present acts the part of a "carrier of oxygen" by undergoing reductions and successive re-formations:—

The influence of steam in determining the explosion of carbonic oxide and oxygen has since been confirmed by several experimenters; but, as some* discussion has arisen as to the *mode* in which the steam exerts its influence, I venture to bring before the Society the reasons which appear to me to show that the hypothesis referred to gives the simplest explanation of the observed facts.

Starting on the assumption that dry carbonic oxide and oxygen do not explode, and that the presence of a minute trace of steam confers inflammability on the mixture, I will examine some of the methods by which the steam may be supposed to exert its influence.

The first question to be asked is—Does the steam act in virtue of some property peculiar to itself, or does it share this catalytic power with other gases? To answer this question, the following experiments were made:—Small quantities of different gases were added to separate portions of a non-inflammable mixture of dry carbonic oxide and oxygen, and the spark was then passed. In all cases where a gas containing hydrogen was introduced, the mixture exploded; in all cases where a gas containing no hydrogen was introduced, the mixture did not explode. This argument by the *Joint*

* See Prof. Armstrong's address to Chemical Section of British Association at Aberdeen.

Method becomes stronger the greater the number of instances, positive and negative, adduced, and the nearer the positive and negative instances are in kind to each other. In the following table, under "positive instances" is given the composition of those gases, the presence of which determined the explosion of dry carbonic oxide and oxygen; under "negative instances" is given the composition of those gases which did not determine the explosion:—

Positive instances.	Negative instances.
H ₂ O	SO ₂ .
H ₂ S	CS ₂ .
H ₄ C ₂	CO ₂ .
H ₂ CO ₂	N ₂ O.
H ₃ N	C ₂ N ₂ .
H ₁₂ C ₅	CCl ₄ .
HCl	

Thus whilst an oxide of hydrogen and sulphide of hydrogen both determined the explosion, a third gas composed of sulphur and oxygen did not; whilst a sulphide of hydrogen and a carbide of hydrogen both determined the explosion, a third gas composed of sulphur and carbon did not. Oxygen, sulphur, carbon, nitrogen, and chlorine when combined one with the other, had no action; the same elements combined with hydrogen determined the explosion. Thus only steam—or bodies which form steam under the conditions of the experiment—were found capable of determining the explosion; other gaseous bodies, which differ from the former in not forming steam, were found to have no action. The conclusion is irresistible that the steam does not act as a mere "third body," but, in virtue of its own peculiar chemical properties.

It being shown, then, that steam determines the explosion of carbonic oxide and oxygen in virtue of its chemical properties, the second question is—Does the steam act in some unknown way, by its presence, without undergoing chemical change, or does it undergo a cycle of chemical reactions whereby it gives up oxygen to the carbonic oxide, and returns to its original state? To this question, I believe, no

absolute answer can be given with our present knowledge, for we have no *direct* evidence that the steam is chemically changed during the explosion. But if it can be shown that such a cycle of chemical reactions can take place under the conditions of the experiment, then it is reasonable to prefer an explanation which accounts for the action by known forces, to an explanation which involves the existence of unknown forces. Such a cycle *can* occur, and, as I shall show later on, there is strong experimental evidence against the mere "contact" action of steam.

What then are the reactions by which steam can convey oxygen to carbonic oxide? My hypothesis is that the carbonic oxide is oxidised by the steam in the path of the spark, and that the hydrogen set free unites with oxygen to form steam at a high temperature; the steam so produced acts on more carbonic oxide, and so on, until all the oxygen or carbonic oxide is used up. It is necessary for this complex change that carbonic oxide should decompose steam at the temperature reached in the explosion, and that hydrogen should unite with oxygen under the same conditions. These two reactions are fundamental. If either of them is proved not to occur under the conditions of the experiment, the hypothesis falls to the ground. In a memoir "On the Conditions of Chemical Change in Gases" (*Phil. Trans.*, 1884), I brought forward experiments which appeared to me to establish these two reactions: for (1) when carbonic oxide was exploded with defect of oxygen in a moistened eudiometer, the carbonic acid formed was found to be more than twice the oxygen used, and a corresponding quantity of free hydrogen was found to be present in the residue; and (2) in a dry mixture of hydrogen and oxygen an electric spark caused an explosion under a pressure exactly as low as in a damp mixture. But in a recent paper read before the German Chemical Society, Moritz Traube has rejected my explanation on the ground that carbonic oxide does not decompose steam at a high temperature; and he has put forward the hypothesis that the steam determines the explosion by a joint action with the carbonic oxide on the oxygen, whereby the steam is oxidised to hydrogen peroxide, and the carbonic oxide to carbonic acid:—

and that the peroxide of hydrogen is then reduced to steam by more carbonic oxide:—

Moritz Traube says:—

"When moist carbonic oxide is submitted to the action of induction sparks for several hours, its volume is not altered, and no trace

of carbonic acid and hydrogen are formed. In opposition to Dixon's supposition, hydrogen has the reverse action on carbonic acid, reducing it at a white heat; for if electric sparks are continuously passed through a mixture of carbonic acid and hydrogen, carbonic oxide and steam are formed with a corresponding diminution of volume."

In these positive statements, Traube asserts not only that carbonic oxide does not decompose steam at the temperature caused by the passage of the induction spark, but he argues that the reaction is impossible because the reverse action occurs under the same conditions. I will first deal with these two statements, and afterwards discuss his own explanation.

1. *The Action of Steam on Carbonic Oxide in contact with Red-hot Platinum.*

The oxidation of carbonic oxide by steam at a high temperature was discovered by Grove. In the paper read before the Royal Society in 1846, "On certain Phenomena of Voltaic Ignition and the Decomposition of Water by Heat," which formed the Bakerian Lecture for 1847, Grove describes two experiments which completely refute Traube's statements. These two experiments seem to have been obscured by the brilliant discovery to which they led—the decomposition of water at a high temperature. I can find no mention of them in any of the chemical manuals I have consulted. Bunsen when he made his experiments on the incomplete combustion of gases, was unaware of the oxidation of carbonic oxide by steam in an explosion. In 1876 the reaction was rediscovered independently by Horstmann and myself in repeating Bunsen's experiments. In the work I have lately been engaged in—viz., heating a coil of platinum wire first in carbonic oxide and steam, and then in carbonic acid and hydrogen, I have been unconsciously repeating the experiments made by Grove 40 years ago. Employing the current from the nitric acid battery he had invented a few years previously, Grove heated a loop of platinum wire sealed into a glass eudiometer containing various gases :—

"Hydrogen and carbonic acid mixed in equal volumes were readily acted on by the ignited wire; they contracted to 0.48 of the original volume; the residue was carbonic oxide; one equivalent of oxygen had therefore united with the hydrogen.

"Carbonic oxide exhibited a remarkable effect, and one which, coupled with the last experiment, gave rise to considerations which mainly led to the results to be detailed in the body of

this paper. Carbonic oxide, very pure, and carefully freed from carbonic acid, was exposed to the ignited wire over distilled water; the gas increased in volume in one experiment to one-third of its original volume—in the greater number of instances to one-fifth: this increase depended upon the intensity of ignition, which it was very difficult to maintain at its maximum on account of the frequent fusions of the platinum wires.

“Here again I had a long research—and many erroneous guesses—which I need not detail. The effect did not take place with perfectly dry gas over mercury, and I thence was led to attribute it to some combination with aqueous vapour; the increase turned out to be occasioned by the formation of carbonic acid. By agitation with caustic potash or lime-water the gas was reduced to exactly its original bulk, but it was now found to be mixed with a volume of hydrogen equal to the volume of carbonic acid by which it had been increased; it was thus perfectly clear that half a volume of oxygen derived from the vapour of the water had combined with one volume of carbonic oxide, and formed one volume of carbonic acid, leaving in place of the carbonic oxide with which it had combined the one volume of hydrogen with which it had been originally associated.

“Comparing the last experiment, viz., that of mixed carbonic acid and hydrogen with this, I was naturally struck with the curious reversal of affinities under circumstances so nearly similar; in the one case hydrogen taking oxygen from carbonic acid to form water, and leaving carbonic oxide; in the other, carbonic oxide taking oxygen from water to form carbonic acid and leaving hydrogen.”

This “curious reversal of affinities” led Grove to test the stability of steam at a high temperature—an investigation which is classical in chemistry. The facts themselves are explained by the “Law of Mass.” When carbonic oxide and steam are heated they react to form carbonic acid and hydrogen; the carbonic acid and hydrogen so produced react to form carbonic oxide and steam. At a certain point in the decomposition (depending on the conditions of the experiment) the rate of decomposition is equalled by the rate of recombination; the mixture then remains in equilibrium. So that if a platinum wire is heated in a mixture of carbonic oxide and steam, carbonic acid and hydrogen are produced. As the carbonic oxide and steam are exhausted, the rate of this change becomes slower; but as the carbonic acid and hydrogen increase, the rate of the inverse change becomes quicker. An equilibrium is therefore reached when the two inverse changes take place at equal rates, and it is immaterial which pair of

gases are present to start with; the same equilibrium is reached when carbonic oxide is heated in steam, or carbonic acid is heated in hydrogen.

The carbonic oxide employed in the following experiments was prepared from anhydrous magnesium formate; the carbonic acid was prepared by the action of dilute hydric sulphate on powdered Iceland spar; the oxygen by heating well-dried potassium chlorate: the hydrogen by electrolysis of dilute hydric sulphate. The gases were collected over mercury and dried by anhydrous phosphoric acid.

Into a straight glass eudiometer two coils of platinum were attached to thick platinum pieces, AA', BB', sealed into the glass. A current from three Grove cells served to heat both coils to bright redness. A small ring of gas-jets, C, surrounding the eudiometer served to keep hot the top of the mercury column and the glass between the mercury and the coils.

In the first experiment the current was diminished until the coils were just invisible in the dark. The volume of carbonic oxide and steam remained unaltered. When the coils were visible in the dark a very slight expansion was noticed. On heating the coils to dull redness the volume gradually increased and became constant after four hours. On passing up into the tube a few drops of a dilute solution of potash the gases contracted to their original volume.

Expt. 1. Pressure 600 mm.

Platinum Coils heated in Carbonic Oxide and Steam to Dull Redness.

Volume of dry gas reduced to 0° and 760 mm.		Percentage.
Vol. of carbonic oxide at starting ..	22·20 c.c.	100·0
After heating for 1 hour	22·55 „	101·6
„ „ 2 hours	22·91 „	103·2
„ „ 4 „	23·35 „	105·2
„ „ 6 „	23·35 „	105·2
After adding potash.....	22·24 „	100·2

This experiment shows that out of 100 volumes of carbonic oxide, 5·2 volumes were converted into carbonic acid with the liberation of 5·2 volumes of hydrogen.

Expt. 2. Pressure 600 mm.

Platinum Coils heated in Carbonic Oxide and Steam to Redness.

Volume of dry gas reduced to 0° and 760 mm.		Percentage.
Vol. of carbonic oxide at starting ..	23·87 c.c.	100·0
After heating for 1 hour	25·55 „	107·0
„ „ 4 hours	26·66 „	111·7
„ „ 6 „	26·64 „	111·6
After adding potash.....	23·87 „	100·0

Eudiometer with Platinum Coils.

Expt. 3. Pressure 600 mm.

Platinum Coils heated in Carbonic Oxide and Steam to Bright Redness.

Volume of dry gas reduced to 0° and 760 mm.		Percentage.
Vol. of carbonic oxide at starting ..	24.94 c.c.	100.0
After heating 4 hours	28.52 „	114.3
After adding potash	24.97 „	100.1

These experiments show that steam begins to oxidise carbonic oxide at a dull red heat, and that at a bright red heat about one-sixth the carbonic oxide is converted into carbonic acid.

2. *The Action of Hydrogen on Carbonic Acid in contact with Red-hot Platinum.*

In a second series of experiments, equal volumes of dry carbonic acid and hydrogen were brought into the eudiometer, and the two coils were heated in the same way as before.

Platinum Coils heated in Carbonic Acid and Hydrogen to Bright Redness.

Volume of dry gas reduced to 0° C. and 760 mm.		Percentage.
Vol. of carbonic acid.....	15.04 c.c.	100.0
„ hydrogen	15.04 „	100.0
Total	30.08 „	200.0
After heating for 1 hour	19.66 „	130.7
„ „ 4 hours.....	17.15 „	114.0
„ „ 12 „	17.08 „	113.6

On heating the coils, the hydrogen reduces the carbonic acid with the formation of steam and carbonic oxide, the volume of the dry gas therefore diminishes.

In this experiment, in which carbonic acid and hydrogen were taken to start with, the final equilibrium was practically the same as in the previous experiment in which the initial gases were carbonic oxide and steam.

The *limited* reduction of carbonic acid by hydrogen in presence of the products of their reaction serves to confirm, instead of to disprove, the oxidation of carbonic oxide by steam.

In both these experiments, it is possible to push the reaction further by removing one of the products of the change. For instance when steam acts on carbonic oxide and the carbonic acid is removed as it is formed, the whole of the carbonic oxide can be oxidised; and, conversely, when hydrogen acts on carbonic acid and the steam is removed as it is formed, the whole of the carbonic acid can be reduced.

3. *Action of Steam on Carbonic Oxide in presence of Potash.*

Three similar eudiometers, each fitted with a single coil of platinum wire, were charged with an equal volume of carbonic oxide. Some dilute solution of potash was introduced into the three tubes, and the wires were heated. After four hours' heating, the gases in the first tube were analysed; after 16 hours' heating, the gases in the second tube were analysed; and after 64 hours' heating, the gases in the third tube were analysed.

	1. After 4 hours' heating.	2. After 16 hours' heating.	3. After 64 hours' heating.
Carbonic oxide ..	75·2	39·5	29·9
Hydrogen	24·8	60·5	70·1
	<hr/> 100·0	<hr/> 100·0	<hr/> 100·0

In a second experiment, a eudiometer with two coils was used, and the wires were kept hotter than in the previous series. After four hours' heating, one-third of the gases was removed, and the remainder was heated for 12 hours longer. Then half this remainder was removed, and the residue was heated for 16 hours longer.

	1. After 4 hours' heating.	2. After 16 hours' heating.	3. After 32 hours' heating.
Carbonic oxide ..	15·0	2·8	0·8
Hydrogen	85·0	97·2	99·2
	<hr/> 100·0	<hr/> 100·0	<hr/> 100·0

These experiments show that, when the carbonic acid formed is removed from the sphere of action, carbonic oxide may be entirely oxidised by excess of steam.

4. *Action of Hydrogen on Carbonic Acid in presence of Anhydrous Phosphoric Acid.*

Dry carbonic acid was mixed with an excess of dry hydrogen in the eudiometer, and several short sticks of anhydrous phosphoric acid were introduced into the gases. After the volume of the gases had been measured, the coils were heated to redness. From time to time the eudiometer was cooled and the contraction observed. After heating for 40 hours, all but 0·4 per cent. of the carbonic acid had been reduced.

Platinum Coils heated to Redness in Carbonic Acid and Hydrogen in presence of P₂O₅.

	Volume of dry gas reduced to 0° and 760 mm.	Percentage.
Vol. of carbonic acid.....	9·49 c.c.	100·0
Vol. of hydrogen	14·67 „	154·6
	<hr/>	
Total	24·16 „	254·6
After heating for 40 hours	14·71 „	155·0
	<hr/>	<hr/>
Contraction	9·45 „	99·6

5. *The Action of Induction Sparks on Carbonic Oxide and Steam.*

The fact that steam oxidises carbonic oxide when induction sparks are passed through the mixed gases was discovered by Buff and Hofmann,* who also confirmed Grove's observation that an incandescent platinum wire transforms carbonic oxide, when confined over water, into carbonic acid. Buff and Hofmann give no numbers. In repeating these experiments, sparks from an induction coil were passed through carbonic oxide and steam between two spheres of platinum-iridium 2 mm. apart. The volume increased rapidly at first, but after an hour remained nearly constant. On adding potash, after 12 hours' sparking, the gases contracted to less than their original volume, showing that some other gas besides carbonic acid had been formed. The solution was tested, and was found to give all the reactions of a formate.

Volume of dry gas reduced to 0° and 760 mm.		Percentage.
Vol. of carbonic oxide at starting ..	18·80 c.c.	100·0
After 1 hour sparking	19·48 „	103·6
After 12 hours' sparking	19·60 „	104·3
After adding potash	15·78 „	83·9

In another experiment, a large Leyden jar was connected with the secondary coil of the Ruhmkorff, and very powerful sparks were passed from this apparatus through the mixture of carbonic oxide and steam. The mixture expanded to about the same extent as before, but the glass near the wires was covered with a thick black deposit, which proved to be nearly all carbon. On heating the deposit in the air it glowed and disappeared, leaving a small grey metallic residue, no doubt volatilised from the wires. When potash solution was added to the mixture, the gases, as before, contracted to less than their original volume; but the solution when tested showed that not more than a trace of formate was present. Some carbonic oxide had, therefore, been decomposed with the formation of carbon and carbonic acid. It appears from this experiment that the decomposition of carbonic oxide, which quickly reaches its limit in the dry gas,† takes place to a much larger extent when the liberated oxygen is removed by union with undecomposed carbonic oxide in presence of steam.

* "On the Decomposition of Gaseous Compounds." Buff and Hofmann (*J. Chem. Soc.*, 12, 282).

† When sparks from a Leyden jar were sent through dry carbonic oxide, a slight decomposition took place amounting to about 0·5 per cent. of the original gas.

Powerful Sparks through Carbonic Oxide and Steam.

	Volume reduced to 0° and 760 mm.	Percentage.
Vol. of carbonic oxide at starting ..	22.66 c.c.	100.0
After 16 hours' sparking.....	23.72 „	104.7
After addition of potash	19.45 „	85.8

In another experiment, sparks from the Leyden jar were passed for one hour through carbonic oxide and steam; the volume expanded about 4 per cent., but no trace of formate could be detected in the tube.

6. The Action of Induction Sparks on Carbonic Acid and Hydrogen.

When induction sparks were passed through a mixture of carbonic acid and hydrogen, in which the hydrogen was in slight excess, the volume quickly contracted, and after three hours only 6.4 per cent. of the carbonic acid remained undecomposed, as shown by the contraction on adding potash. A trace of formate was found in the solution, so that the carbonic acid remaining was probably less than 6 per cent. The sparking caused a very slight yellow deposit on the glass near the wires.

	Volumes reduced to 0° C. and 760 mm.	Percentage.
Vol. of carbonic acid at starting ..	22.86 c.c.	100.0
Vol. of hydrogen at starting	23.37 „	102.2
Total	46.23 „	202.2
Vol. after 1 hour sparking	25.05 „	109.6
„ 3 hours' sparking	24.70 „	108.0
„ adding potash	23.24 „	101.6
Contraction on adding potash.....	1.46 „	6.4

7. The Incomplete Combustion of Carbonic Oxide in presence of varying Quantities of Steam.

At the beginning of this paper, I mentioned an experiment which showed that when carbonic acid was exploded with insufficient oxygen to completely burn it in a moist eudiometer, the excess of carbonic oxide reacted with the steam at the high temperature produced to form carbonic acid and hydrogen. With the small quantity of steam present at ordinary temperatures, only a small quantity of free hydrogen is so produced; but by raising the temperature of the eudiometer the proportion of steam can be increased at pleasure, and a proportionately large quantity of hydrogen is then found in the residue. A mixture of carbonic oxide and oxygen was made in the

proportion of about 3 to 1. Half of this mixture was fired in a eudiometer saturated with steam at 52°C .; the second half of the mixture was fired under the same pressure, but saturated with steam at a temperature of 68° . The number of steam molecules in the first case was half that of the oxygen; in the second case the number of steam molecules present was the same as that of the oxygen. In the following table the results of these experiments are given, together with those of the original experiment at the ordinary temperature.

Expt. 1.

At 15° . Tension of Steam 13 mm.

Before the explosion.			After the explosion.		
CO.	O ₂ .	H ₂ O.	CO ₂ .	CO.	H ₂ .
273·7	100	10?	203	70·7	3·0

Analysis of Residue.

	Found.	Calculated.
CO	70·7	70·7
H ₂	2·9	3·0

Expt. 2.

At 52° . Tension of Steam 102 mm.

Before the explosion.			After the explosion.		
CO.	O ₂ .	H ₂ O.	CO ₂ .	CO.	H ₂ .
296·8	100	50	211·4	85·4	11·4

Analysis of Residue.

	Found.	Calculated.
CO	85·2	85·4
H ₂	11·6	11·4

Expt. 3.

At 68°. Tension of Steam 214 mm.

Before the explosion.			After the explosion.		
CO.	O ₂ .	H ₂ O.	CO ₂ .	CO.	H ₂ .
296·8	100	100	221·1	75·7	21·1

Analysis of Residue.

	Found.	Calculated.
CO	76·0	75·7
H ₂	21·4	21·1

Although some of the water on the sides of the eudiometer was no doubt evaporated during these explosions, and took part in the reaction, the experiments bring out clearly the fact that as the quantity of steam is increased the quantity of carbonic oxide oxidised by it increases also. In the last experiment more than 10 per cent. of the carbonic acid formed was owing to the action of the steam on the carbonic oxide.

It has thus, I think, been amply proved by different experimenters that when steam and carbonic oxide are heated together, either by an induction spark or by a red-hot coil of platinum, or by heated gases in their neighbourhood—the steam oxidises some of the carbonic oxide; and, if fresh proof were required, it has been afforded in a paper (*Ber.*, 1885, 2894) just published by Naumann and Pistor. Since my experiments were made, these chemists have shown that when carbonic oxide and steam are heated in a tube below 580° no reaction takes place; a little above 600° the action begins, and at 950° 10½ per cent. of the carbonic oxide is oxidised to carbonic acid.*

Traube's Hypothesis.

That a trace of peroxide is found on the sides of a moistened jar held over a lighted jet of carbonic oxide is put forward by Traube as

* Under other conditions the equilibrium may be very different. Thus Maquenne (*Compt. rend.*, 96, 63) found that when carbonic oxide and steam were submitted to the silent electric discharge at a low pressure, 96 to 97 per cent. of the carbonic oxide was turned into carbonic acid.

evidence that the burning of carbonic oxide is brought about by the formation and decomposition of peroxide of hydrogen according to the two equations—

Now as Traube considers that peroxide is invariably formed when hydrogen burns with oxygen, the fact of peroxide being produced when carbonic oxide burns in the air might equally well have been used by him as an argument that there is hydrogen uniting with oxygen in the flame, and that, therefore, the steam had been decomposed by the carbonic oxide. But as Traube had (wrongly) concluded that carbonic oxide does not decompose steam at a high temperature, such an interpretation was not open to him.

The fact that hydrogen peroxide is found under the conditions of Traube's experiment is no proof that the carbonic oxide is oxidised by peroxide of hydrogen; the evidence advanced for such a reaction is no stronger than could probably be advanced for several other reactions. For instance, formic acid is produced when induction sparks are passed through carbonic oxide and steam; formic acid is oxidised to steam and carbonic acid by oxygen; and *dry* carbonic oxide and oxygen explode in presence of formic acid. These are facts which might be urged with at least equal plausibility to show that carbonic oxide is oxidised by the alternate formation and decomposition of formic acid according to the equations—

This interpretation, however, of the function of the steam is not open to us, because it has been shown that formic acid is not produced either by a very powerful spark or by a red-hot platinum wire in carbonic oxide and steam, whereas both the powerful spark and the red-hot wire cause the explosion of moist carbonic oxide and oxygen.

The formation of hydrogen peroxide under the conditions described by Traube seems to be due to the heating of the water by the carbonic oxide flame burning in air, as I shall show in Part II.

PART II.—THE ACTION OF HYDROGEN ON OXYGEN.

The hypothesis I have put forward as to the manner in which the presence of steam determines the explosion of carbonic oxide and oxygen has thus been verified to this extent—that some of the steam present would certainly be decomposed in the region of ignition, with the formation of carbonic acid and free hydrogen. It remains to

answer the question, Does this hydrogen unite directly with the oxygen present to form steam? Traube, who finds that peroxide of hydrogen is formed in considerable quantity when the steam from a hydrogen flame is rapidly condensed, by making the lighted jet dip into water, concludes that hydrogen and oxygen do not unite directly to form steam, but that they either react directly to form peroxide of hydrogen, or that hydrogen, oxygen, and steam react together to form water and the peroxide, which is in either case then decomposed by hydrogen :—

It is certainly true that hydrogen peroxide is formed in considerable quantity when a lighted jet of hydrogen dips into pure water. I have confirmed this observation of Traube's several times. But it is also equally true that a lighted jet of pure cyanogen gas playing on the surface of pure water produces a considerable quantity of hydrogen peroxide. Now, I have found that cyanogen, *carefully dried by anhydrous phosphoric acid*, burns in air or oxygen, the presence of steam being unnecessary for its combustion. The formation of hydrogen peroxide appears, therefore, to be due to the heating effect of the cyanogen flame; and the same explanation accounts for its formation by a lighted jet of hydrogen or of carbonic oxide. The following experiment shows that when a portion of pure water is evaporated in air, hydrogen peroxide is found in the residue. 10 c.c. of pure water quite free from peroxide was heated in a porcelain crucible by means of hot sand. No flame or burning body was near the crucible. When 8 c.c. had evaporated the residue gave the reactions of hydrogen peroxide strongly marked. It would seem, then, that the formation of hydrogen peroxide is due to a secondary reaction, and no argument as to the union of oxygen and hydrogen can be drawn from its presence in condensed steam.

I have found that a mixture of hydrogen and oxygen dried by long contact with anhydrous phosphoric acid is exploded by the passage of an electric spark between terminals either of platinum, or of silver, or of aluminium. The platinum terminals had been previously heated in oxygen in presence of phosphoric acid, the silver terminals had been previously heated in hydrogen in presence of phosphoric acid, and the aluminium terminals had been subjected to both processes, for the purpose of preventing the formation of steam at the passage of the spark by hydrogen or oxygen occluded in the metal. A platinum coil, previously heated to whiteness in oxygen in presence of phosphoric acid, when raised to a red heat, after the addition of hydrogen, instantly exploded the mixture. Although

these experiments do not show conclusively that hydrogen unites directly with oxygen at a high temperature without the intervention of steam, I think they make it *probable* that both under the influence of the spark, and in the presence of red-hot platinum, hydrogen and oxygen do unite directly. Once the reaction is begun, no other steam but that being formed in the reaction is necessary to propagate the explosion. There can be no doubt, I think, on this point. For (1) when a mixture of hydrogen and oxygen has its pressure gradually raised until a spark causes an explosion, the pressure at which it inflames is the same whether the mixture be well dried or damp; and (2) the explosion travels as fast in a well-dried mixture as in a damp mixture. Again, the experiments of Berthelot and Vieille (*Compt. rend.*, 95, 151) have shown that the rate of the "explosive wave" in hydrogen and oxygen is identical with the mean velocity of translation of the *steam* molecules formed in the reaction at the maximum temperature of the explosion. This result I have recently confirmed by a concordant series of measurements (*Brit. Assoc. Reports*, 1885).

These experiments show that when hydrogen and oxygen are exploded in a tube, each successive layer is brought to the ignition point by the impact of steam molecules from the layer just burnt. The rate of the explosive wave corresponds with the velocity of *steam* molecules, and not with the velocity of *hydrogen peroxide* molecules, or with a velocity intermediate between these two. Hydrogen appears, therefore, to unite directly with oxygen to form steam when the temperature of the mixture is raised; at all events the reaction takes place *in the presence of steam*.

The hypothesis of alternate reduction and oxidation by which I have explained the action of the steam on carbonic oxide and oxygen has thus been verified to the further extent, that each part of the process has been separately verified. It has been shown that, *under the conditions of the experiment, carbonic oxide is oxidised by steam with the liberation of hydrogen, and that hydrogen unites with oxygen to re-form steam.*

It yet remains to show that these two reactions give the best explanation of the phenomena exhibited in the incomplete combustion of mixtures of carbonic oxide and hydrogen.

The Incomplete Combustion of Carbonic Oxide and Hydrogen.

The experiments of Horstmann (*Annalen*, 190, 228; *Ber.*, 10, 1626; 12, 64) and myself (*Phil. Trans.*, 1884, Part II) on the incomplete combustion of carbonic oxide and hydrogen have, I think, shown conclusively that the final division of the oxygen between the two combustibles depends on an equilibrium being established between the

two opposite chemical changes—the oxidation of carbonic oxide by steam and the reduction of carbonic acid by hydrogen. In this paper, a similar equilibrium has been shown to be established when mixtures either of carbonic oxide and steam, or carbonic acid and hydrogen, are heated by a platinum wire.

Though the establishment of these reactions removes the chief argument for Traube's hypothesis, it might yet be urged that the union of oxygen with carbonic oxide and hydrogen takes place by means of hydrogen peroxide, and that the reactions determining the above equilibrium in an explosion are *subsequent* to the oxidation of the carbonic oxide and hydrogen by the peroxide. The phenomena observed in the incomplete combustion of carbonic oxide and hydrogen are not in accordance with this view.

When a mixture of carbonic oxide and hydrogen is exploded with insufficient oxygen for complete combustion, at a temperature at which no condensation of steam can take place during the reaction, and at a pressure greater than the critical pressure, the product of the carbonic oxide and steam molecules remaining bears a constant ratio to the product of the carbonic acid and hydrogen molecules remaining, whatever the quantities of carbonic oxide and hydrogen taken to start with, and whatever the quantity of oxygen employed, so long as the oxygen taken is less than half the hydrogen:—

$$\frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}} = 4.$$

When the oxygen employed is more than half the hydrogen, then the ratio between the two products (or the coefficient of affinity) is diminished.

My experiments have shown that when a certain percentage of oxygen is used, the proportion of the hydrogen to the carbonic oxide may be continually reduced without altering the coefficient of affinity, until the hydrogen is reduced to *twice* the oxygen; at that point the coefficient drops, and slowly diminishes as the proportion of hydrogen is further reduced. When a different percentage of oxygen is employed, the same phenomena occur; the coefficient is constant until the hydrogen is reduced to *twice* the oxygen, and then the coefficient drops as before. By varying the percentage of oxygen used the lowering of the coefficient may be made to occur with very different proportions of hydrogen in the mixture; and since in all cases the lowering occurs where the hydrogen and oxygen are present in the proportion of 2 to 1, the one fact is shown to be necessarily connected with the other.

Now, this alteration of the coefficient, when the oxygen is just equal to half the hydrogen, follows as a natural consequence from the

hypothesis that the carbonic oxide is oxidised by the alternate reduction and re-formation of steam; it receives no explanation on the hypothesis that carbonic oxide is oxidised by the alternate formation and reduction of peroxide of hydrogen.

The presence of an inert gas, such as nitrogen, among the combustible gases is found to favour the formation of carbonic acid instead of steam, and therefore to lower the coefficient. If the carbonic oxide receives its oxygen only from the steam formed, it follows that when the oxygen taken is more than half the hydrogen, there will be present during part of the reaction an excess of oxygen chemically indifferent to the three other gases present, viz., carbonic oxide, carbonic acid, and steam, and it will only be capable of reacting as the steam is gradually decomposed by the carbonic oxide. No doubt the molecules of steam, as they are first formed, begin to react on the carbonic oxide, but the formation of steam in an explosion is much faster than the formation of carbonic acid, so that during a period which may be a considerable fraction of the whole time during which the gases are reacting, the excess of oxygen is present as an inert gas, diminishing the intensity of the reaction, like nitrogen, and so favouring the formation of carbonic acid. We should expect then to find a lowering of the coefficient to occur whenever the proportion of oxygen approaches to half the hydrogen.

Now, what should be expected if peroxide of hydrogen were the carrier of oxygen? If we suppose with Traube that the oxygen unites simultaneously with hydrogen and steam, and with carbonic oxide and steam, forming steam, carbonic acid, and peroxide of hydrogen:—

and that the peroxide is reduced both by the carbonic oxide and hydrogen in excess:—

then, even if the formation of steam is considerably faster than that of carbonic acid, there will be no *inert* oxygen present during the reaction, for the oxygen will always be in the presence of carbonic oxide and steam, with which it can combine directly. No lowering of the coefficient ought, therefore, to occur. The same argument tells against the "contact theory" of the action of steam in determining the explosion of carbonic oxide and oxygen. If steam acted by its mere presence without entering into chemical reactions with the carbonic oxide and oxygen, there is no apparent reason for a sudden

change in the coefficient, for steam is present in all cases, and sometimes in larger proportion with the lowered coefficient than when the coefficient is normal.

On the other hand, accepting Traube's alternative view that the oxygen unites directly with hydrogen to form peroxide of hydrogen, then, if this reaction is the first to take place, we might expect to find, in the absence of steam, an excess of oxygen *inert* to the remaining gases, viz., carbonic oxide and hydrogen peroxide, and only gradually entering into combination as *steam* was liberated from the peroxide by the action of the carbonic oxide. But in this case the lowering of the coefficient ought to occur when the volume of oxygen is *equal* to the volume of hydrogen taken, and not when it is *half* the hydrogen.

POST SCRIPTUM.—Professor Armstrong's ingenious suggestion that, in a mixture of carbonic oxide and oxygen, the carbonic oxide is oxidised, and the oxygen is hydrogenised simultaneously by the steam present is not, I think, opposed to any of the observed facts. It would account for the lowering of the "coefficient of affinity," when the oxygen is more than half the hydrogen in the incomplete combustion of a mixture of carbonic oxide and hydrogen, if we suppose that the oxygen molecules are unable to react except when they meet with both carbonic oxide and steam molecules simultaneously. Professor Armstrong's explanation involves the simultaneous occurrence of the two reactions which I consider occur successively.